U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-247 699

REPORT ON THE PROBLEM OF HALOGENATED AIR POLLUTANTS AND STRATOSPHERIC OZONE

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY

PREPARED FOR
COMMITTEE ON INTERSTATE AND FOREIGN COMMERCE,
(U.S. HOUSE OF REPRESENTATIVES)

DECEMBER 1975

KEEP UP TO DATE

Between the time you ordered this report—which is only one of the hundreds of thousands in the NTIS information collection available to you—and the time you are reading this message, several *new* reports relevant to your interests probably have entered the collection.

Subscribe to the **Weekly Government Abstracts** series that will bring you summaries of new reports *as soon as they are received by NTIS* from the originators of the research. The WGA's are an NTIS weekly newsletter service covering the most recent research findings in 25 areas of industrial, technological, and sociological interest—invaluable information for executives and professionals who must keep up to date.

The executive and professional information service provided by NTIS in the **Weekly Government Abstracts** newsletters will give you thorough and comprehensive coverage of government-conducted or sponsored research activities. And you'll get this important information within two weeks of the time it's released by originating agencies.

WGA newsletters are computer produced and electronically photocomposed to slash the time gap between the release of a report and its availability. You can learn about technical innovations immediately—and use them in the most meaningful and productive ways possible for your organization. Please request NTIS-PR-205/PCW for more information.

The weekly newsletter series will keep you current. But *learn what you have missed in the past* by ordering a computer **NTISearch** of all the research reports in your area of interest, dating as far back as 1964, if you wish. Please request NTIS-PR-186/PCN for more information.

WRITE: Managing Editor
5285 Port Royal Road
Springfield, VA 22161

Keep Up To Date With SRIM

SRIM (Selected Research in Microfiche) provides you with regular, automatic distribution of the complete texts of NTIS research reports *only* in the subject areas you select. SRIM covers almost all Government research reports by subject area and/or the originating Federal or local government agency. You may subscribe by any category or subcategory of our WGA **(Weekly Government Abstracts)** or **Government Reports Announcements and Index** categories, or to the reports issued by a particular agency such as the Department of Defense, Federal Energy Administration, or Environmental Protection Agency. Other options that will give you greater selectivity are available on request.

The cost of SRIM service is only 45¢ domestic (60¢ foreign) for each complete microfiched report. Your SRIM service begins as soon as your order is received and processed and you will receive biweekly shipments thereafter. If you wish, your service will be backdated to furnish you microfiche of reports issued earlier.

Because of contractual arrangements with several Special Technology Groups, not all NTIS reports are distributed in the SRIM program. You will receive a notice in your microfiche shipments identifying the exceptionally priced reports not available through SRIM.

A deposit account with NTIS is required before this service can be initiated. If you have specific questions concerning this service, please call (703) 451-1558, or write NTIS, attention SRIM Product Manager.

This information product distributed by

NTIS U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
5285 Port Royal Road
Springfield, Virginia 22161

353067

PB 247 699

EPA-600/9-75-008
December 1975

REPORT ON THE PROBLEM OF HALOGENATED AIR POLLUTANTS AND STRATOSPHERIC OZONE

PRICES SUBJECT TO CHANGE

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
US Department of Commerce
Springfield, VA. 22151

Environmental Sciences Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

65

TECHNICAL REPORT DATA
(Please read instructions on the reverse before completing)

1. REPORT NO. EPA-600/9-75-008	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE REPORT ON THE PROBLEM OF HALOGENATED AIR POLLUTANTS AND STRATOSPHERIC OZONE		5. REPORT DATE December 1975 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) ORD and OAWM Staff		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Sciences Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711		10. PROGRAM ELEMENT NO. 1AA008 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, N.C. 27711		13. TYPE OF REPORT AND PERIOD COVERED Final 14. SPONSORING AGENCY CODE EPA-ORD

15. SUPPLEMENTARY NOTES
Prepared for and submitted to the Subcommittee on Public Health and Environment, Committee on Interstate and Foreign Commerce, House of Representatives

16. ABSTRACT

EPA is conducting a research program on halocarbon air pollutants and their possible interaction with stratospheric ozone. Principal compounds under study are fluorocarbon-11, fluorocarbon-12, fluorocarbon-22, carbon tetrachloride, methyl chloroform, perchloroethylene, trichloroethylene, dichloroethane, methylene dichloride, and methyl chloride. Laboratory studies concern the rates of decomposition of these pollutants in the air and the identity and fate of their decomposition products. Field studies involve measuring concentrations of halocarbons and their decomposition products as functions of altitude and distance from sources. Fluorocarbons are discussed in detail, with regard to emission sources, current control technology, and possible chemical substitutes. Problems of emissions control and EPA's regulatory authority are reviewed and the economic impacts of several regulatory options for fluorocarbons are considered.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
* Halohydrocarbons * Stratosphere * Ozone * Depletion Air pollution Problem solving		07C 04A 07B

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 64
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (9-73)

EPA-600/9-75-008
December 1975

REPORT ON THE PROBLEM OF HALOGENATED AIR POLLUTANTS AND STRATOSPHERIC OZONE

submitted to

Subcommittee on Public Health and Environment
Committee on Interstate and Foreign Commerce
U. S. House of Representatives

U. S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

DISCLAIMER

This report has been reviewed by the Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

PREFACE

This report was submitted in September, 1975, to the Subcommittee on Public Health and Environment, Committee on Interstate and Foreign Commerce, House of Representatives. It discusses the potential problem of ozone depletion in the stratosphere resulting from the release of some halogenated hydrocarbons, and presents knowledge gaps existing in EPA research activities and plans for future research.

This report was prepared by Dr. Aubrey P. Altshuller, Director, and Dr. Philip L. Hanst, Senior Research Scientist, in the Environmental Sciences Research Laboratory. Mr. Kenneth H. Lloyd, Office of Air Quality Planning and Standards, provided the information presented in Appendix B.

The Chemistry and Physics Advisory Committee and staff members of the Office of Research and Development and Office of Air and Waste Management reviewed the report and offered a number of worthy comments.

CONTENTS

		Page
Preface		iii
Summary		
List of Figures		vi
List of Tables		vi
I	Introduction	1
II	Production, Uses, and Emissions of Halogenated Compounds	4
III	The Research and Development Program in EPA	6
	Program description	6
	The results of field measurements	6
	The results of laboratory studies	7
IV	Atmospheric Chemistry Summary	14
	Chlorinated compounds	14
	A comment on brominated compounds	14
	Natural emissions	14
V	Emission Control - Needs and Problems	19
	Degree of Threat of Major Halogenated Pollutants	19
VI	Regulatory Authorities of EPA	25
VII	Research Needs	26
	Atmospheric measurements	26
	Measurement techniques	27
	Laboratory studies	29
VIII	References	31
Appendix A:	Summary of EPA Research Program on Halogenated Air Pollutants-August 1975	32
Appendix B:	Preliminary Assessment of Economic Impact of Alternatives to Control Fluorocarbon Emissions to the Atmosphere	36

Preceding page blank

LIST OF FIGURES

Number		Page
1	World-wide chlorine content of major man-made chlorinated pollutants - 1973	17
2	World-wide amounts of chlorine in halogenated compounds after photooxidation in troposphere and lower stratosphere - 1973	17
3	Materials flow chart for chlorocarbons	21

LIST OF TABLES

Number		Page
1	Estimated Emissions of Halogenated Compounds into the Atmosphere	5
2	Atmospheric Chemistry Summary	15

SUMMARY

The Environmental Protection Agency is actively studying certain aspects of the problem of the interaction of halogenated chemical species with stratospheric ozone. The halogenated gaseous pollutants contain fluorine, chlorine, and/or bromine. About 20 percent of the pollutants of concern are the fully halogenated compounds such as fluorocarbon-11, fluorocarbon-12, and carbon tetrachloride. No known ways exist by which these pollutants are removed from the lower atmosphere by ground surfaces or oceans. Consideration of chemistry and physical transport models indicate that fully halogenated substances migrate to the stratosphere where they are photodissociated, with consequent adverse effects predicted on the ozone balance. Fully halogenated substances have been measured in the stratosphere.

The remaining 80 percent of the emissions of halogenated pollutants involve production and usage losses of various high production industrial organic chemicals including methyl chloroform, methylene dichloride, dichloroethane, perchloroethylene, trichloroethylene, vinyl chloride, and smaller amounts of other chlorinated and brominated industrial chemical. The chemistry of these compounds is such that they have shorter lifetimes in the lower atmosphere than the fully halogenated compounds. However, the lifetimes of these compounds, or the lifetimes of halogenated compounds formed by chemical reactions, may be long enough for a significant fraction of the compounds to move into the stratosphere along with the fully halogenated compounds. If so, they will likely undergo the same type of reactions, thus also contributing to potential ozone depletion.

In addition to the urgent need for a continuing program to measure fluorocarbon-11 and fluorocarbon-12, continuing study of other halogenated pollutants by EPA is needed. This research will include studies of tropospheric removal processes and their rates as well as stratospheric photodissociation processes and their rates. These studies should be directed at both the parent compounds and oxidation products.

Optical and gas chromatographic measurements of atmospheric pollutants should be carried out as functions of altitude, latitude, and time. Measurements are needed of the potential for removal by rain of a number of these halogenated substances and their halogenated reaction products. Laboratory studies must be addressed to unknown factors that limit the accuracy of the modeling of atmospheric chemical processes. These factors include photooxidation mechanisms, rates of individual oxidation reaction steps. photodissociation rates and products, and hydrolysis rates and products. The Office of Research and Development of EPA is addressing these needs for atmospheric measurements and laboratory studies.

If continuing research confirms the danger of stratospheric ozone depletion by halogenated pollutants, control measures will be necessary. Use of fluorocarbons as aerosol propellants would have to be curtailed.

Fluorocarbons used in refrigeration applications would have to be replaced by other working fluids that are not detrimental to the environment. Halogenated pollutants emitted during industrial operations would have to be controlled by best available control technologies such as vapor recovery, solvent recycling, or the substitution of alternate compounds. Considerations of atmospheric chemistry and health effects would determine which alternate compounds were acceptable.

The current research program funded by EPA is described in Appendix A of this report. Appendix B covers emission sources, current control technology, and possible chemical substitutes for the fluorocarbons. The economic impacts of several regulatory options for fluorocarbon are considered.

SECTION I
INTRODUCTION

This report pertains to a potential problem concerning depletion of stratospheric ozone by air pollutants containing chlorine, fluorine, and bromine. Some researchers have predicted that ozone depletion would increase the incidence of skin cancer and might affect climate and crops. The possible effects have been discussed in the report of the Federal Task Force on Inadvertent Modification of the Stratosphere (IMOS) issued in June 1975.[1]

At hearings before the Subcommittee on Public Health and Environment, Committee on Interstate and Foreign Commerce, House of Representatives on December 11, 1974, Mr. John R. Quarles, Jr., Deputy Administrator of the Environmental Protection Agency indicated that EPA would report by August 1975 on progress in its research program on halogenated air pollutants. This report therefore focuses on EPA activities. It supplements the IMOS report and is independent of the study of fluorocarbons by the National Academy of Sciences. The main concern of the EPA program and this report is to bring out certain aspects of the overall problem that need consideration if EPA must take future action to regulate production or usage of fluorocarbons and other halogenated pollutants.

Stratospheric ozone depletion by halogenated pollutants involves the following chemical sequence. A chlorine atom released in the stratosphere attacks ozone, yielding chlorine oxide and diatomic ozygen. The chlorine oxide reacts with oxygen atoms that exist in photochemical equilibrium with ozone. This reaction yields diatomic oxygen and regenerates a chlorine atom that is then free to attack another ozone molecule.

$$Cl + O_3 \rightarrow ClO + O_2$$

$$O_3 + h\nu \rightarrow O_2 + O$$

$$ClO + O \rightarrow O_2 + Cl$$

This sequence will repeat itself hundreds or thousands of times until the chlorine atom is removed from the scene in a collision with a hydrogenated molecule such as methane,

$$Cl + CH_4 \rightarrow HCl + CH_3$$

Fluorine atoms released into the ozonosphere will undergo a similar sequence of reactions, but with a much shorter chain length. The

chain is shorter in the fluorine case because the chain-breaking hydrogen abstractions are faster. The halogen acids HCl and HBr can also return their halogen atoms to the ozone cycle in reactions with OH radicals: $HCl + OH \rightarrow H_2O + Cl$. Hydrogen fluoride does not undergo this return reaction.

Bromine atoms will initiate a similar sequence, with chains longer than those involving chlorine.

The rate of input of halogen atoms to the stratosphere must be established if the ozone depletion predictions are to be accepted as reliable. This rate of input depends on two main factors: (1) the transport of the halogenated pollutants through the troposphere and stratosphere, and (2) atmospheric chemical reactions during transport.

Most of the scientific effort by other government agencies and industry is presently associated with transport and reaction processes in the stratosphere. This aspect received considerable discussion in the IMOS report and no doubt will also be discussed in the NAS report. Therefore, the present EPA program and this report do not emphasize stratospheric monitoring or models of stratospheric processes, but address questions concerning the possible role of each of the major fluorocarbon and halocarbon pollutants and to problems associated with the control of these emissions.

Concern extends not only to the major fluorocarbons in commercial production, but also to a substantial number of other chlorine-containing and bromine-containing pollutants. Fluorocarbons of concern are fluorocarbon-11 (CCl_3F), fluorocarbon-12 (CCl_2F_2), fluorocarbon-22 ($CHClF_2$), fluorocarbon-113 ($C_2Cl_3F_3$), and fluorocarbon-114 ($C_2Cl_2F_4$). The other halogenated pollutants include methyl chloride, methylene chloride, chloroform, carbon tetrachloride, ethyl chloride, ethylene dichloride, methyl chloroform, vinyl chloride, trichloro-ethylene, perchloroethylene, methyl bromide, and ethylene dibromide. Any of these major pollutants could have an adverse effect on the stratosphere if the atmospheric residence time of either the pollutant molecule or its reaction product is long enough to allow penetration of the stratosphere. As usage patterns shift, additional compounds should come under consideration. Emissions inventories indicate that methylene dichloride, ethylene dichloride, methyl chloroform, vinyl chloride, trichloroethylene, and perchloroethylene are each lost to the atmosphere in amounts equal to or exceeding the fluorocarbons. Large amounts of carbon tetrachloride were lost to the atmosphere from early in the present century up to the 1960's when its general use, other than as a starting material for fluorocarbons, was largely eliminated.

Measurements show that most of the carbon tetrachloride still resides in the atmosphere. Some halocarbons, such as vinyl chloride and trichloroethylene are known to have residence times much too short to reach the stratosphere in significant amounts. Other halocarbons have intermediate but inadequately determined residence times. Practically none of the chlorinated photooxidation products have had their residence times determined.

Recent experimental results indicate the existence of large biogenic sources of methyl chloride and methyl bromide. The impact of natural sources of halogen atoms on the stratospheric ozone balance has to be taken into consideration. Therefore, the worldwide distributions and residence times of the naturally emitted halocarbons must be accurately determined.

If research demonstrates that individual halocarbons have significant potential for stratospheric depletion of ozone, then emission abatement options may be considered for implementation.

A number of optional strategies are available for control of fluorocarbons and halocarbons. These strategies are associated closely with the usage pattern of each individual halocarbon, the potential for reducing emissions through technology or with use of alternative means of providing an acceptable end product.

SECTION II
PRODUCTION, USES, AND EMISSIONS OF HALOGENATED COMPOUNDS

Data on world-wide production, end-use, and estimated emissions of the principal halogenated air pollutants for the year 1973 are given in Table 1. This tabulation has been extracted from a report prepared by Arthur D. Little, Inc. under contract to the Environmental Protection Agency, Office of Air Quality Planning and Standards. That report, entitled Preliminary Economic Impact Assessment of Possible Regulatory Action to Control Atmospheric Emissions of Selected Halocarbons, is currently in process of publication.[2] Emissions of brominated halocarbons have not been precisely defined and are not tabulated. They appear to be small compared to the emissions of chlorinated compounds.

Present world-wide production and emission occurs roughly 50 percent in the United States, 35 percent in Europe, and 15 percent in the rest of the world. From the table it is seen that the 1973 emissions were proportioned 20 percent fluorocarbons, and 80 percent other chlorinated pollutants. These figures emphasize the importance of a careful consideration of the possible impact of these other chlorinated pollutants on the stratospheric ozone, as discussed in the following sections.

Table 1. ESTIMATED EMISSIONS OF HALOGENATED COMPOUNDS INTO THE ATMOSPHERE

Compound	World production in 1973, millions of pounds	Principal uses (and percent of total production)	Estimated emissions into the atmosphere in 1973	
			World total, millions of pounds	U.S. total, percent
Fluorocarbon-11	670	Aerosol propellant (78%)	600	50
Fluorocarbon-12	980	Aerosol propellant (47%) Refrigerant (34%)	740	50
Fluorocarbon-22	270	Refrigerant (66%)	120	50
Fluorocarbon-113	110	Solvent (85%)	100	50
Fluorocarbon-114	100	Propellant (91%) Refrigerant (9%)	70	50
Carbon tetrachloride	2090	Production of fluorocarbons (88%)	88	50
Chloroform	496	Production of fluorocarbons (90%)	12	50
Ethyl chloride	1210	Produce tetraethyl lead (85%)	29	55
Ethylene dichloride	26,400	Produce vinyl chloride (78%)	1250	35
Methyl chloride	880	Produce silicones (43%) and tetramethyl lead (38%)	11	60
Methyl chloroform	900	Metal cleaning (70%) and degreasing	835	60
Methylene chloride	935	Paint remover (40%)	760	55
Perchloroethylene	1650	Dry cleaning (65%)	1370	45
Trichloroethylene	1540	Metal cleaning (86%)	1390	30
Vinyl chloride	15,600	Produce polyvinyl chloride (89%)	774	25

SECTION III
THE RESEARCH AND DEVELOPMENT PROGRAM IN EPA

PROGRAM DESCRIPTION

The Environmental Sciences Research Laboratory of the Office of Research and Development, EPA, Research Triangle Park, North Carolina, has been engaged in the study of halogenated air pollutants for three years. Until recent months the program has been limited to two university research grants and a small amount of intramural experimental work involving two scientists on a part-time basis. Our interest in the problem goes back to 1971 when the first measurements of halogenated pollutants became known to us.[3][4] At that time, the threat of stratospheric ozone depletion by chlorine atoms had not been recognized. Nevertheless, a modest program of study was initiated, with the long range goals of learning the eventual fate of the halogenated pollutants and determining if any undesirable effects existed.

The detection of the halogenated pollutants had also led a number of other research groups into the study of the possible effects of the pollutants. Rowland and Molina, working under an Atomic Energy Commission research grant at the University of California, Irvine, were especially successful in developing an insight into the possible consequences of the chlorinated pollutants.[5] Their publications in 1974, and the publications of several other groups of researchers, pointed out the potential dangers of stratospheric chlorine-ozone reactions. As a result, government agencies with an interest in the problem, including NASA, NOAA, and EPA, initiated new programs of study. In the latter part of Fiscal Year 1975, the EPA program was expanded to four university grants, a three man-year level of research effort by a contractor at Research Triangle Park, and a three man-year level of effort by our own research staff. A program summary is included as an appendix to this report.

The EPA program has had two aspects: (1) field measurements of the halogenated pollutants, and (2) laboratory studies of the chemical reactions that the pollutants undergo in the atmosphere. Following is a discussion of the results obtained in these studies.

THE RESULTS OF FIELD MEASUREMENTS

In the program of field measurements, gas chromatographic techniques have been applied by Rutgers University personnel and infrared absorption techniques have been applied by EPA personnel. These two measurement programs have made valuable contributions to the existing state of knowledge of the concentrations and spatial distributions of the halogenated pollutants. The detailed results of this work are in process of being published.[6][7] In summary,

the measurements show a spatial distribution of pollutants that can be accounted for in terms of emissions patterns, atmospheric transport properties, and atmospheric chemical reactions.

Chemically inert pollutants such as fluorocarbon-11, fluorocarbon-12, and carbon tetrachloride, are found to be distributed throughout the atmosphere. In the clean air of rural areas, following the passage of a storm front, one sees the true background concentrations of these pollutants. The observed amounts of the three compounds are approximately equivalent to an accumulation of all of man's releases of these compounds up to the present time. There is no firm evidence that any of the three is produced by natural processes. In urban areas, the concentrations of fluorocarbon-11 and fluorocarbon-12 usually are 5 to 10 times greater than their background concentrations, while the concentration of carbon tetrachloride in urban air is usually not higher than its background level. This confirms that fluorocarbon-11 and fluorocarbon-12 are presently being released by the populace, while carbon tetrachloride is not. Present releases of CCl_4 are primarily industrial.

Changes in concentrations of fluorocarbon-11 and fluorocarbon-12 from day to day parallel the changes in auto exhaust pollution. These changes in general pollution level are directly related to the meteorological conditions. When the lower atmosphere stagnates, all the pollutants build up, even in rural areas. When a front moves through vertical mixing seems to dissipate all pollution.

Halogenated pollutants that can be oxidized in the troposphere are not ubiquitous, but show variations in concentration from near zero in rural areas to high values in the vicinity of the sources. Among the oxidizable compounds are the halogenated olefins and the halogenated paraffins with one ore more hydrogens remaining in the molecule.

All of the major suspected halogenated pollutants have been detected either by the gas chromatographic method or by the infrared absorption method. At present there is a great need to increase the sensitivity of these measurements and to carry them out fully as a function of altitude and latitude. The principal species that are yet to be detected are the relatively stable intermediate oxidation products such as phosgene and chloroacetyl chloride. The measurement needs will be discussed more fully in a following section.

THE RESULTS OF LABORATORY STUDIES

The attack of halogen atoms on stratospheric ozone is triggered by photodissociation or photooxidation of the halogenated pollutants. The flux of halogen containing compounds into the stratosphere depends on the chemical stability of the primary halogenated pollutants as well as on the types of chemical transformations that those pollutants undergo, and finally on the chemistry of the reaction products. The reaction steps and rate constants obtained from laboratory measurements thus are basic inputs to the mathematical models of the strato-

spheric chemistry. The ozone loss predictions of these models are strongly dependent on the input rate constants, pollutant concentrations and pollutant spatial distributions. The chemical processes have been a major subject of the Environmental Sciences Research Laboratory program. The work has been carried out in two projects: the research grant at the Pennsylvania State University and the intramural program at Research Triangle Park. Some of the experimental results have been published and others are in the process of publication.[8][9]

The experimental results and some of their implications are discussed below for each principal compound, in alphabetical order. The atmospheric chemistry in these discussions is based on information available at the present time. Since there are gaps and uncertainties in that body of information, some of the interpretations as to lifetimes, mechanisms, and product yields are only tentative. As the research program continues, the details of the atmospheric chemistry will become more quantitative and more reliable.

Carbon Tetrachloride

The annual release of carbon tetrachloride pollution is small compared to the annual releases of some of the other chlorinated compounds. Nevertheless, the inertness of carbon tetrachloride has allowed the compound to accumulate in the air so that it is a major halogenated pollutant. There are no indications of CCl_4 removal processes at work in the troposphere. As in the cases of fluorocarbon-11 and fluorocarbon-12, the only suspected removal process is the photodissociation that takes place in the stratosphere. It is likely that this photodissociation occurs in a region where the chlorine atoms are highly effective in destroying ozone. The following three equations summarize the degradation mechanism indicated by laboratory studies:

$$CCl_4 + h\nu \rightarrow CCl_3 + Cl$$

$$CCl_3 + O_2 \rightarrow COCl_2 + ClO$$

$$COCl_2 + h\nu \rightarrow CO + 2Cl$$

Since the phosgene ($COCl_2$) is a stronger ultraviolet absorber than the carbon tetrachloride, the phosgene photolysis will follow the carbon tetrachloride photolysis rather quickly. Thus all four chlorine atoms will be released into the stratosphere in the vicinity of the initial photolytic dissociation.

Carbon tetrachloride has been a major halogenated pollutant longer than any other. Consequently, it seems possible that the compound is approaching a steady-state distribution throughout the troposphere and stratosphere. Carbon tetrachloride may therefore be the halogenated pollutant having the greatest present effect on stratospheric ozone. The future threat of carbon tetrachloride, however, is not rated as great as the future threat of fluorocarbon-11 and fluorocarbon-12, because the present emission rate of CCl_4 is relatively small.

Chloroform

Chloroform is a minor chlorinated pollutant, subject to photo-oxidation in the troposphere. The abstraction of the hydrogen from the molecule by OH radicals leaves a CCl_3 radical which reacts with oxygen to yield phosgene, ($COCl_2$), and chlorine oxide (ClO). The atmospheric lifetime of chloroform is estimated to be two or three months. Thus the chlorine oxide will be released in regions of the atmosphere where there is very little ozone to be destroyed. Before any ozone is encountered, the ClO will be reduced to Cl, and the Cl will abstract hydrogen from methane yielding hydrogen chloride. This HCl will be removed in precipitation. The phosgene must of course be considered for its potential interaction with ozone. If this phosgene were to migrate to the ozone-rich regions of the stratosphere, its photodissociation would contribute to ozone destruction. Phosgene removal processes and their rates need to be established for both the troposphere and the stratosphere.

Ethyl Chloride

The impact of ethyl chloride on stratospheric ozone may be considered negligible for two reasons: (1) the amount of ethyl chloride emitted is relatively small, and (2) the compound will largely be photooxidized in the troposphere, yielding up its chlorine in the form of hydrogen chloride. The hydrogen chloride will be removed from the atmosphere either by direct interaction with the earth's surface or by absorption in precipitation.

Ethylene Dichloride (1,2 Dichloroethane)

Ethylene dichloride is emitted to the atmosphere in large amounts. The compound may be a threat to stratospheric ozone by virtue of yielding chloroacetyl chloride during photochemical oxidation. If this product is formed in the lower troposphere it will probably be washed out by rain. If it forms in the stratosphere, however, the chloroacetyl chloride may persist until its chlorine is released in photodissociation. Available data on the rate of reaction of ethylene dichloride with hydroxyl radicals indicate an atmospheric lifetime of three or four months. This might be long enough to allow some ethylene dichloride to penetrate the stratosphere. Further study of this reaction rate should be undertaken. Attempts should be made to measure both the ethylene dichloride and the chloroacetyl chloride in the stratosphere.

Fluorocarbon-11 (Trichlorofluoromethane)

Fluorocarbon-11 has no recognized removal paths within the troposphere. Stratospheric photodissociation is considered to be the only significant removal process.

$$CCl_3F + h\nu \rightarrow CCl_2F + Cl$$

The released chlorine atoms react with a large number of ozone molecules before being removed as HCl. The CCl_2F radicals react with oxygen to yield ClO and carbonyl chloro fluoride, COClF. The latter

compound is then photolyzed to CO, F, and Cl. The result is that the three chlorine atoms and one fluorine atom are released into the atmosphere in the vicinity of the initial photodissociation.

Fluorocarbon-12 (Dichlorodifluoromethane)

Photodissociation in the stratosphere is the only recognized reaction of dichlorodifluoromethane (fluorocarbon 12) leading to its removal from the atmosphere. The initial photolytic process is written:

$$CCl_2F_2 + h\nu \rightarrow CClF_2 + Cl$$

The chlorine atoms will then attack ozone. The free radical $CClF_2$ will add oxygen and split out ClO, leaving carbonyl fluoride just as in the case of photooxidation of F-22. In the F-12 case, however, the carbonyl fluoride will not be washed out, but instead it will be photodissociated to fluorine atoms and carbon monoxide. The chlorine and fluorine atoms eventually react with hydrogen-containing molecules to yield the halogen acids, HCl, and HF. These travel down to the troposphere and are removed in precipitation.

Fluorocarbon-22 (Chlorodifluoromethane)

Chlorodifluoromethane can have its hydrogen atom abstracted by an OH radical, and therefore will suffer degradation in the troposphere.

$$CHClF_2 + OH \rightarrow H_2O + CClF_2$$

$$CClF_2 + O_2 \rightarrow COF_2 + ClO$$

This OH attack allows an F-22 molecule an atmospheric lifetime of only three or four months. The carbonyl fluoride may be washed out in the troposphere, or it may reach the stratosphere and be photodissociated. Since the amount of chlorine available in fluorocarbon 22 is small and since the chlorine is released mainly in the troposphere, the effect of F-22 on stratospheric ozone is considered minor.

Methyl Chloride

Although methyl chloride is a minor pollutant from the point of view of direct emissions, measurements have shown it to be the halogenated pollutant with the highest background atmospheric concentration. This indicates a natural source, or at least a large indirect human source. It is conceivable that the total emissions of methyl chloride could be carrying into the atmosphere as much chlorine as is carried by all other chlorinated pollutants combined. It thus becomes of great importance to consider the atmospheric chemistry of methyl chloride. The half-life of the compound in the troposphere most likely falls in the range of one to

six months, similar to the half-lives of chloroform and methylene chloride. This may permit some of the methyl chloride to cross into the stratosphere.

The abstraction of a hydrogen atom from methyl chloride has been shown in an EPA study to initiate a series of reactions leading to formyl chloride. The significant finding in this study is that the single chlorine is not released from the molecule as ClO, which can attack ozone, but rather it is released in the carbonyl compound HCOCl. This compound is thermally unstable at room temperature, decomposing to CO and HCl with a half-life of about 20 minutes.

Methyl chloride molecules oxidized in the lower troposphere therefore have little or no potential for destruction of ozone. For oxidation taking place at higher altitudes, the situation may be different. In the upper portion of the troposphere and in the lower stratosphere temperatures can be much lower than room temperature. In these regions the formyl chloride produced in photooxidation may exist long enough to be photodissociated into a chlorine atom and a formyl radical. The best way to determine whether or not reactions are occuring would be to measure methyl chloride in the stratosphere as a function of altitude.

Methyl Chloroform

Methyl chloroform, CH_3CCl_3, is one of the major chlorine carriers in the atmosphere. It is a compound that is rather resistant to photooxidation, with a half-life in the troposphere of several years. Thus it is highly likely that a portion of the methyl chloroform pollution will find its way into the stratosphere. The slow photooxidation that takes place both in the troposphere and in the stratosphere yields trichloro acetaldehyde (chloral). It seems likely that this aldehyde is then oxidized to trichloro acetic acid, although this has not yet been demonstrated experimentally. The acid could be washed out of the troposphere. Both the acid and the aldehyde will be photodissociated in the stratosphere, yielding chlorine atoms that will be free to attack ozone. Methyl chloroform must therefore be considered to be a major threat to stratospheric ozone. The compound should be the subject of further laboratory study and should be measured with care in both the troposphere and stratosphere.

Methylene Chloride

Methylene chloride, CH_2Cl_2, is a major halogenated pollutant with a large potential for delivery of chlorine to the stratosphere. The photooxidation of the compound in the troposphere probably proceeds with a half life of several months, similar to the cases of methyl chloride and chloroform. This half-life may be long enough to allow a substantial part of the methylene chloride to cross the tropopause. The principal oxidation product of methylene chloride is the phosgene which results from the two hydrogens being abstracted from the molecule. It is conceivable that this phosgene may be photolyzed to yield chlorine

atoms in the ozone-rich region of the stratosphere. It thus appears that there is some potential for ozone destruction by methylene chloride. Stratospheric measurements of the parent compound and the phosgene resulting from oxidation are very much needed.

Perchloroethylene

The large release rate of perchloroethylene requires that its removal processes and secondary products be given the most careful study. The attack on the double bond by oxygen atoms, hydroxyl radicals, or ozone molecules produces trichloro acetyl chloride, CCl_3COCl, as a major product and phosgene, $COCl_2$, as a lesser product. The four chlorine atoms confer an oxidation resistance on the molecule, giving it an atmospheric lifetime longer than the lifetimes of most other olefin pollutants. A perchloroethylene molecule may exist in the troposphere for weeks before reacting. A lifetime of weeks is longer than the tropospheric mixing time under certain conditions. Thus, it is possible for perchloroethylene to reach the tropopause and cross into the stratosphere. The important consideration here is not that perchloroethylene may reach the ozone region in the stratosphere--that is unlikely--but rather that the trichloroacetyl chloride and phosgene reaction products may reach the ozone regions. Carbonyl compounds, including phosgene and the chloro acetyl chlorides, are relatively strong absorbers of ultraviolet radiation. Since ultraviolet absorption yields chlorine atoms, it is conceivable that perchloroethylene, through its reaction products, may be influencing the stratospheric ozone balance.

To fully understand the effects of perchloroethylene in the atmosphere, one must determine the fate of the trichloro acetyl chloride and phosgene. Are these compounds washed out of the troposphere by rain? Do they cross the tropopause? Is their rate of photodissociation in the stratosphere slow enough to allow them to reach the layer of high ozone content? These questions must be answered if the role of perchloroethylene in stratospheric chemistry is to be fully understood. Laboratory studies of the removal processes can be helpful, but the best way of determining the role of these reaction products is to directly measure their concentrations in the atmosphere.

Trichloroethylene

Trichloroethylene will be photooxidized in the troposphere with a relatively short half life--less than one day. This, however, does not mean that the compound should be dismissed as a potential source of chlorine atoms in the stratosphere. One needs to consider the reactivity and lifetimes of the chlorinated products of the photooxidation. These products are principally dichloro acetyl chloride and phosgene. The rate of removal of these gaseous compounds needs to be known. This removal may occur at the earth's surface or at the surface of atmospheric particles. Wash-out by rain may be an important process. If these removal rates are slow, it is conceivable that the carbonyl compounds could cross the tropopause and diffuse upwards where they would be photodissociated, yielding chlorine atoms.

Vinyl Chloride

Although a large amount of vinyl chloride is lost to the atmosphere annually, rapid photochemical oxidation removes the compound with a half-life of a few hours. The chlorine separates from the parent molecule either in the form of hydrogen chloride, HCl, or in the form of formyl chloride, HCOCl. The latter compound has been found to decompose thermally with a half-life at room temperature of about 20 minutes, yielding CO and HCl. All the chlorine in vinyl chloride will therefore end up as HCl within a day or two of release. The HCl is removed at surfaces and in precipitation. It is concluded therefore that the impact of vinyl chloride on stratospheric ozone is negligible.

SECTION IV
ATMOSPHERIC CHEMISTRY SUMMARY

CHLORINATED COMPOUNDS

The type of atmospheric degradation of the primary chlorinated pollutants and the proportions of chlorinated reaction products have been determined in the EPA research program. The lifetimes of these pollutants are also fairly well known from EPA studies and from studies in other laboratories. These data are summarized in Table 2. Figure 1 shows a bar graph presentation of the total chlorine content of the pollutants for the year 1973, excluding natural emissions. Figure 2 shows a bar graph of the chlorine content of the primary products that are released by reactions in the troposphere and lower stratosphere, again excluding natural emissions. The fluorocarbon-11, fluorocarbon-12, and carbon tetrachloride are considered to be non-reactive in the troposphere and lower stratosphere. They thus appear in Figure 2 in the same amount as in Figure 1.

A COMMENT ON BROMINATED COMPOUNDS

A bromine atom in the stratosphere may be more damaging to ozone than a chlorine atom, because the removal of bromine by methane is much slower. One must therefore consider whether brominated compounds are finding their way into the stratosphere.

Ethylene dibromide ($C_2H_4Br_2$) is by far the largest commercially produced bromine-containing compound. Its main uses are as a gasoline additive and as a soil and grain fumigant. In the 1960's world production of ethylene dibromide was about 240 million pounds per year. Most of this bromine probably ends up as lead salts that are washed into the ground. If a small fraction of the total entered the atmosphere as ethylene dibromide, however, part of the bromine might be able to reach the stratosphere. This matter should be explored through atmospheric analysis.

Methyl bromide (CH_3Br) is the second principal brominated pollutant. It is mainly used for fumigation of soils and stored commodities to kill rodent and insect pests. Much of this methyl bromide undoubtedly ends up in the atmosphere. Methyl bromide is more expensive than ethylene dibromide, and therefore it is used on a smaller scale. A large amount of methyl bromide may be released along with methyl chloride by the action of marine algae. This matter also needs to be investigated by sensitive atmospheric analysis.

NATURAL EMISSIONS

Natural emissions of methyl chloride are indicated by measurements of background concentrations as high as one part methyl chloride in 10^9 parts air. If this concentration occurs uniformly throughout the atmosphere, and if the tropospheric lifetime of methyl chloride is six months, the influx of methyl chloride into the atmosphere might be on the order of

Table 2. ATMOSPHERIC CHEMISTRY SUMMARY

Compound name and formula	Worldwide release in 1973 of chlorine, 10^9 lbs	Estimated half-life, years	Type of reaction	Tropospheric chlorinated reaction products (and approximate percent of chlorine)	Chlorine in product, 10^9 lbs
Perchloro-ethylene, C_2Cl_4	1.17	0.01	Photooxidation initiated at double bond	Trichloro acetyl chloride (80%)	0.93
				Phosgene (10%)	0.12
				Hydrogen chloride (10%)	0.12
Trichloro-ethylene, C_2HCl_3	1.12	0.001	Photooxidation initiated at double bond	Dichloro acetyl chloride (70%)	0.79
				Phosgene (12%)	0.13
				Formyl chloride (8%)	0.09
				Hydrogen chloride (10%)	0.11
Ethylene di-chloride $C_2H_4Cl_2$	0.90	0.3	Photooxidation initiated by OH abstracting H	Mono chloro acetyl chloride (100%)	0.90
Methyl chloro-form, CH_3CCl_3	0.74	1.1	Photooxidation initiated by OH abstracting H	Trichloro-acetaldehyde (100%)	0.74
Methylene chloride CH_2Cl_2	0.63	0.3	Photooxidation initiated by OH abstracting H	Phosgene (100%)	0.63
Vinyl chloride C_2H_3Cl	0.48	0.0001	Photooxidation initiated at double bond	Formyl chloride (50%)	0.24
				Hydrogen chloride (50%)	0.24

Table 2(cont'd). ATMOSPHERIC CHEMISTRY SUMMARY

Compound name and formula	Worldwide release in 1973 of chlorine, 10^9 lbs	Estimated half-life, years	Type of reaction	Tropospheric chlorinated reaction products (and approximate percent of chlorine	Chlorine in product, 10^9 lbs
Fluorocarbon-11, CCl_3F	0.46	100	Stratospheric photo-dissociation	Fluorocarbon-11 (100%)	0.46
Fluorocarbon-12, CCl_2F_2	0.44	100.	Stratospheric photo-dissociation	Fluorocarbon-12 (100%)	0.44
Carbon tetrachloride, CCl_4	0.084	100	Stratospheric photo-dissociation	Carbon tetrachloride (100%)	0 .084
Fluorocarbon-22, $CHClF_2$	0.050	0.3	Photooxidation initiated by OH abstracting H	Carbonyl fluoride & chlorine monoxide (100%)	0 .050
Ethyl chloride, C_2H_5Cl	0.015	0.3	Photooxidation initiated by OH abstracting H	Formyl chloride (100%)	0.015
Chloroform, $CHCl_3$	0.011	0.2	Photooxidation initiated by OH abstracting H	Phosgene (67%) Chlorine monoxide (33%)	0.008 0.003
Methyl chloride, CH_3Cl	0.007	0.4	Photooxidation initiated by OH abstracting H	Formyl chloride (100%)	0.007

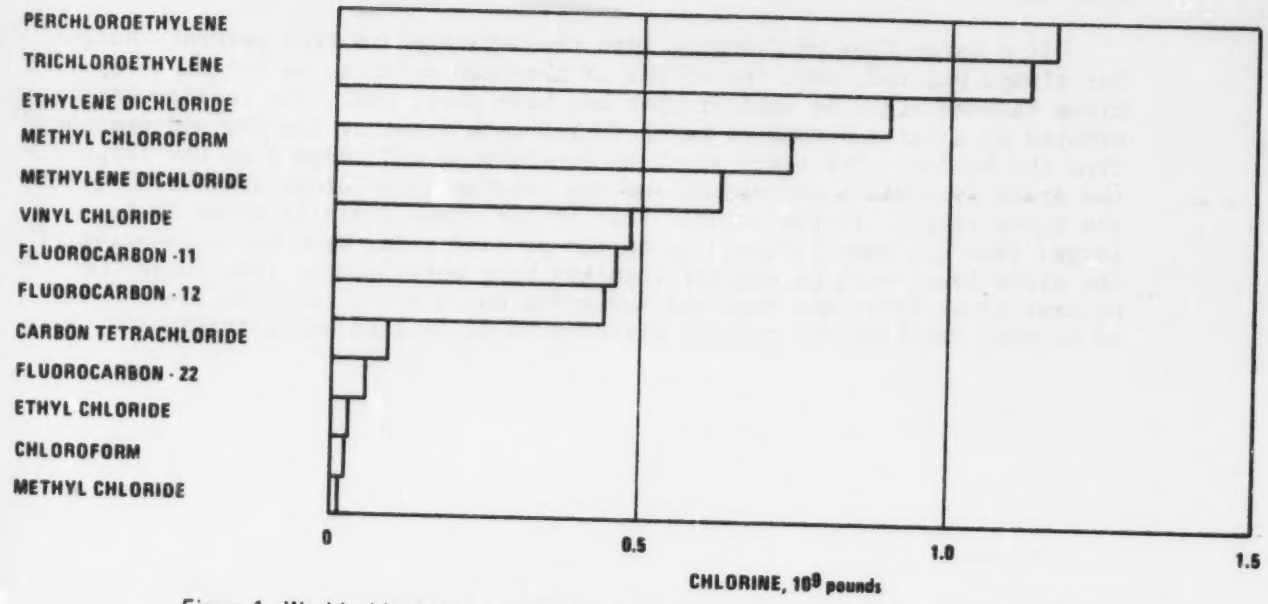

Figure 1. World-wide chlorine content of major man-made chlorinated pollutants - 1973.

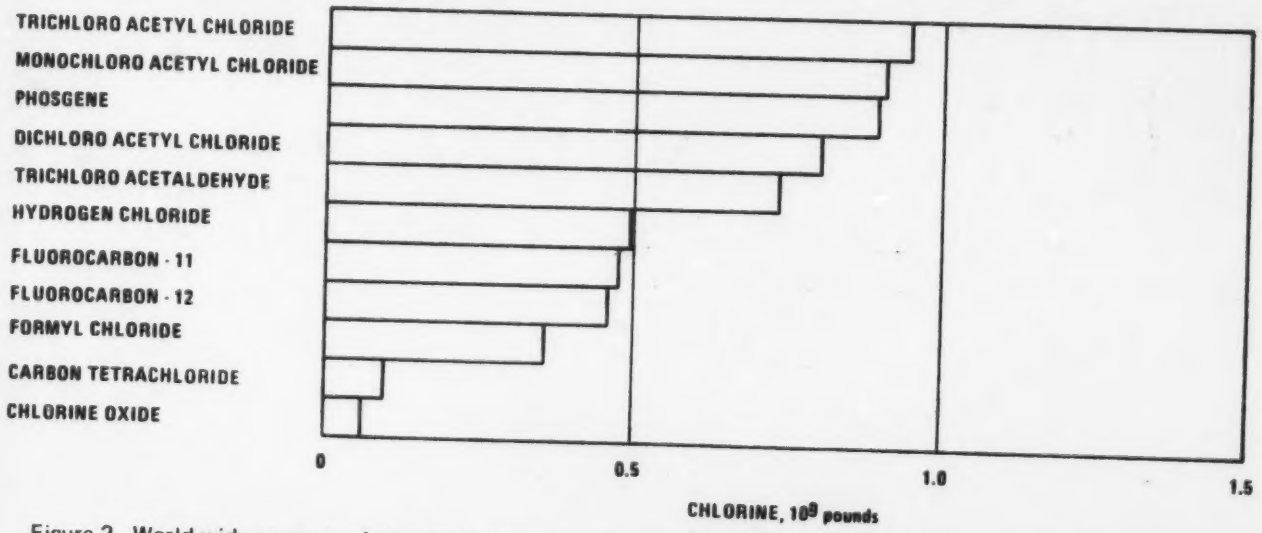

Figure 2. World-wide amounts of chlorine in halogenated compounds after photo-oxidation in troposphere and lower stratosphere - 1973.

fifty billion pounds per year. That much methyl chloride would carry more chlorine than all man-made chlorinated pollutants combined. This matter clearly demands confirmatory atmospheric measurements as well as laboratory studies of methyl chloride photooxidation. If methyl chloride is emitted in such large quantities from natural sources, perhaps methyl bromide is also emitted.

If a large flux of chlorine into the stratosphere from natural sources has always existed, then the effect of man-made chlorine on the stratospheric ozone balance might be smaller than has been predicted. The analogy has been offered of a bathtub that is being filled with water at the top and drained from the bottom. The water level at equilibrium will depend on how large the drain is. Man's enlargement of the stratospheric ozone drain will lower the ozone level. If the natural size of the ozone drain is shown to be larger than has been believed up to the present time, then man's lowering of the ozone level will be smaller than has been anticipated. How large the natural ozone drain has been and how great man's effect will be are subjects of current research and current differences of opinion among scientists.

SECTION V
EMISSIONS CONTROL - NEEDS AND PROBLEMS

The control of emissions of halogenated pollutants may encounter technical difficulties and may cause economic disruptions. It is therefore prudent to consider problems of control now for any compounds that have a reasonable possibility of needing control in the future. Possible economic disruptions are discussed in detail in the report, previously cited, to be issued by the EPA Office of Air Quality Planning and Standards (2). Two summary figures from that report are presented here as Figures 3 and 4. These figures, in the form of flow charts, show the close interrelationships among many of the chlorocarbons, fluorocarbons and other industrial chemicals. These charts show that disruptions in one sector of the chlorocarbon industry are likely to have serious effects in other sectors. The charts also emphasize the important position that chlorocarbons occupy in the chemical industry. Imposition of fluorocarbon or chlorocarbon controls would most clearly cause economic disruptions.

DEGREE OF THREAT OF MAJOR HALOGENATED POLLUTANTS

The need for emissions control obviously must be established with as little uncertainty as possible. It is presumed that if a need is established, control will be imposed, regardless of the difficulties. Current research programs in the United States, including the program of the Environmental Protection Agency, therefore seek to determine the degree of threat to stratospheric ozone posed by each major halogenated pollutant. The current state of knowledge of the atmospheric chemistry and transport processes allows some preliminary conclusions. These are stated below, along with some comments on problems of emissions control. In most cases, the current state of knowledge does not allow firm conclusions, but indicates needs for further study.

Carbon Tetrachloride

Carbon tetrachloride appears to be one of the principal chlorine carriers presently migrating to the stratosphere and interacting with the ozone. Current emissions of CCl_4 are relatively small, so that control of the compound cannot have a large effect on the projected future flux of chlorine atoms into the stratosphere. At the same time it is recognized that any control that can be effected will be of value, especially since CCl_4 contains a higher percentage of chlorine, by weight, than any other chlorinated pollutant.

Home uses of CCl_4 have been severely curtailed because of health hazards. Domestic releases thus are not as great as they once were. Venting of CCl_4 to the atmosphere presently occurs mainly during industrial operations, such as the production of fluorocarbons. Control of these emissions may require revision of manufacturing techniques or installation of vapor recovery equipment. CCl_4 is also lost to the atmosphere in its use as a solvent and as a grain fumigant. These losses may be reduced or eliminated by choosing an alternate compound.

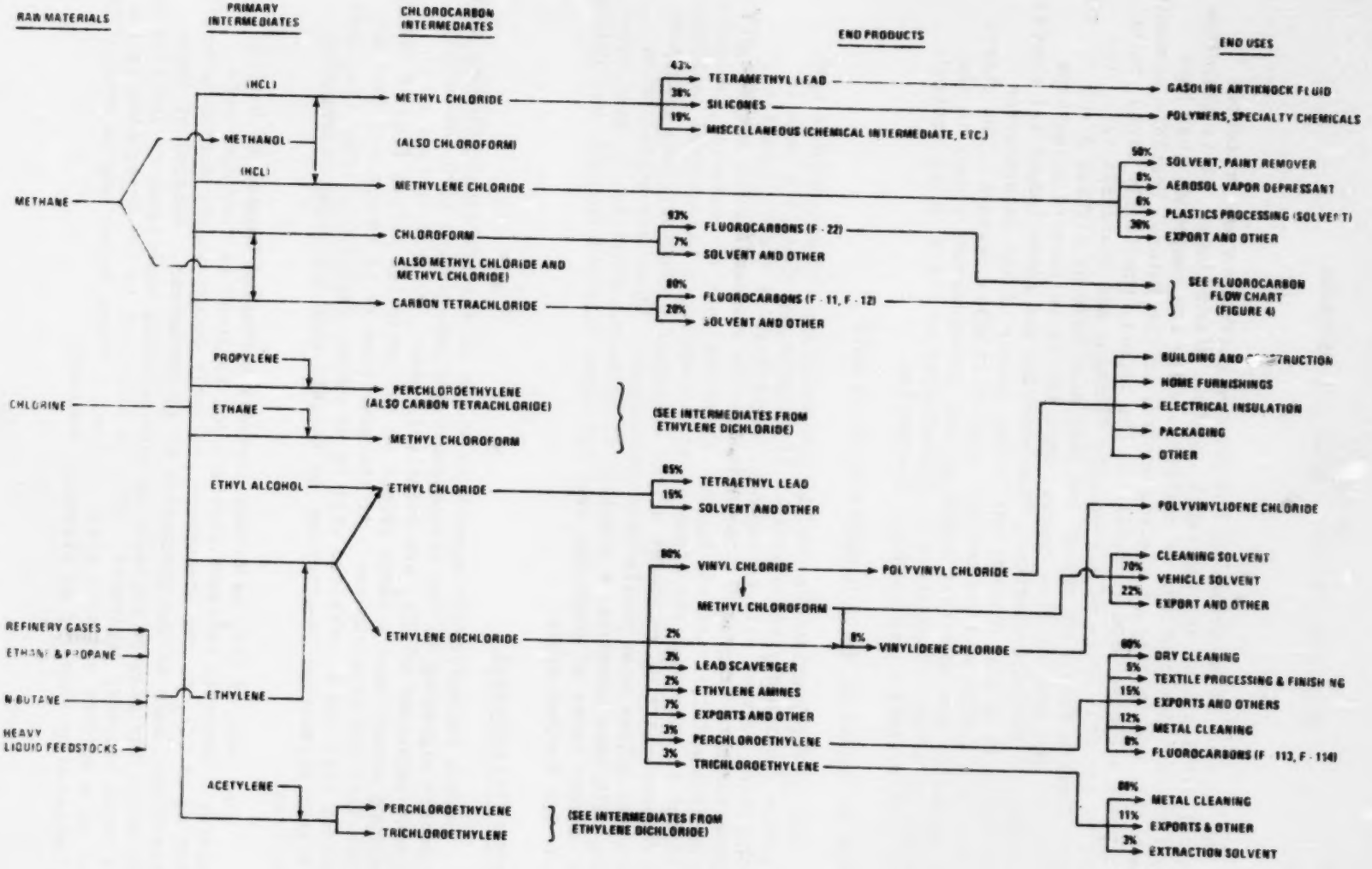

Figure 3. Materials flow chart for chlorocerbons (Source: Arthur D. Little, inc., estimates).

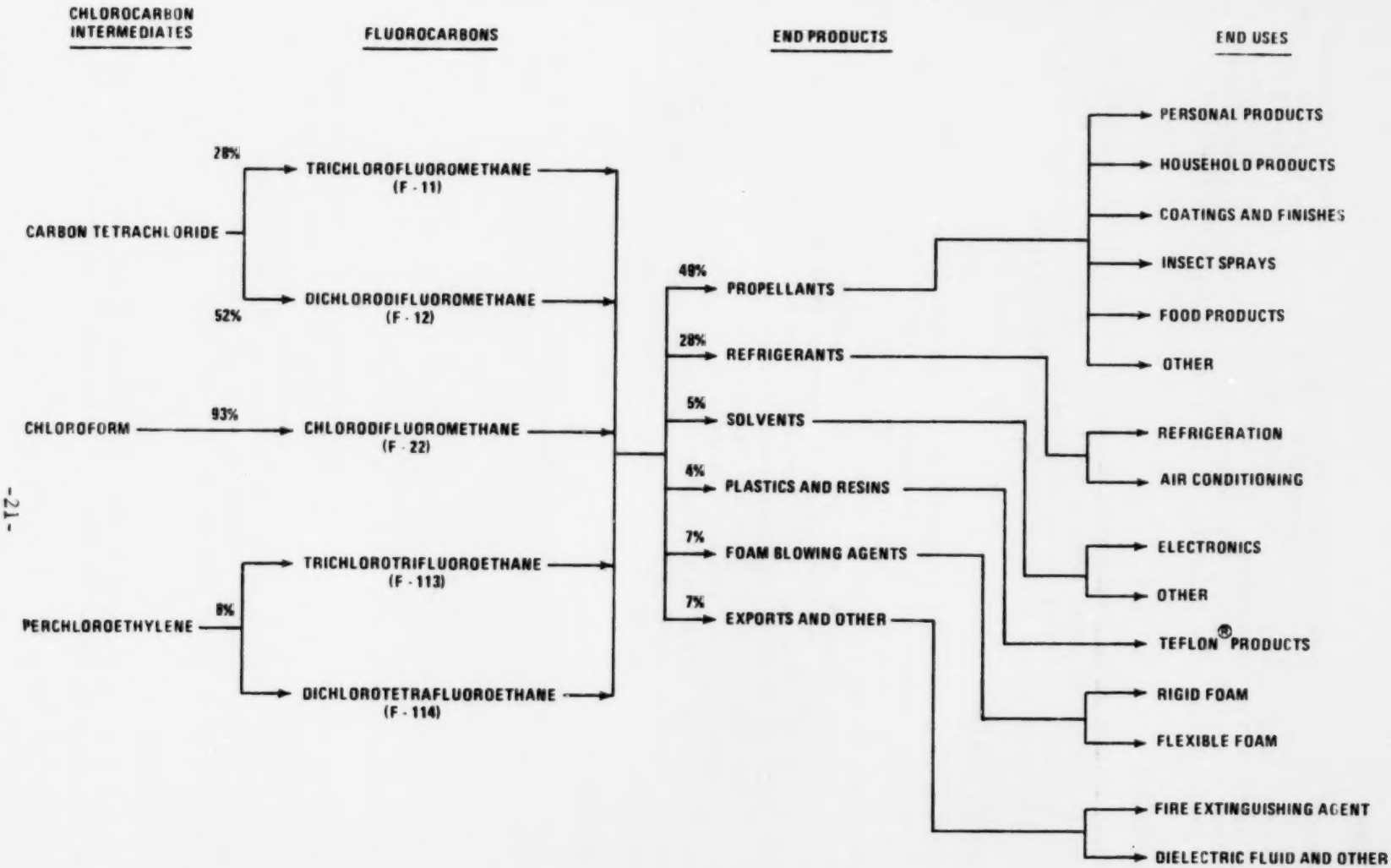

Figure 4. Materials flow chart for fluorocarbons (Source: Arthur D. Little, Inc., estimates).

Chloroform

Control of chloroform emissions would only have a very small effect on the flux of chlorine into the stratosphere. Chloroform is not emitted to the atmosphere in large quantities. The small amount emitted is likely to be photooxidized in the troposphere. If the phosgene reaction product can travel from lower troposphere to stratosphere, there might be some effect on the stratospheric ozone balance, but it would be a small effect.

Ethyl Chloride

There appears to be little need to control ethyl chloride because the compound is emitted in small amounts and it will largely be photo-oxidized in the troposphere, yielding up its chlorine as hydrogen chloride. This HCl will in turn be taken out of the atmosphere by precipitation.

Ethylene Dichloride

Until proven otherwise, ethylene dichloride must be considered a threat to stratospheric ozone. As shown in Figure 3, ethylene dichloride is the precursor of vinyl chloride and other large volume chlorinated compounds. Its production volume is so large that a few percent loss in processing amounts to a large volume of emission into the atmosphere. The lifetime of ethylene dichloride in the troposphere is three or four months--long enough to allow a wide distribution of the compound. The chlorinated reaction product, chloroacetyl chloride, may have sufficient stability to travel upwards to the ozone layer. These are important matters to be addressed in the continuing research program. Meanwhile, the problems of control of ethylene dichloride should be considered. Since the emissions are mainly industrial, controls might take the form of improvements in handling methods, vapor recovery systems, or manufacturing process changes.

Fluorocarbon-11

Since no removal processes have been discovered for fluorocarbon-11 in the troposphere, it must be assumed that stratospheric photo-dissociation is the outlet for all of the chlorine carried into the atmosphere by the compound. This chemical behavior and the large tonnage of F-11 releases have resulted in the compound being ranked as a primary threat to the stratospheric ozone balance. If further atmospheric measurements and laboratory studies fail to alter the prevailing concepts of the role of F-11 in the atmosphere, then control actions should be undertaken.

The major use of F-11 as propellant in personal care products can probably be discontinued with no great hardship to the general public. Alternate methods of delivering hair preparations, deodorants, and insect killers are easy enough to visualize. Non-spray delivery is one possibility; finger pumping is another. If a propellant must be used, other gases such as carbon dioxide can be considered.

Fluorocarbon-12

Fluorocarbon-12 is ranked with fluorocarbon-11 as a primary threat to the stratospheric ozone balance. If this view is maintained through

the current program of atmospheric analysis and laboratory study, emissions control should be undertaken. As in the case of F-11, it appears that the use of F-12 as an aerosol propellant could be phased out by the development of alternate delivery systems and by the substitution of other propellant gases. The replacement of F-12 in refrigeration systems will no doubt take considerably longer than its replacement in propellant applications. A change to other refrigeration working fluids will require new product development by manufacturers--a process that takes a number of years. Among the alternate working fluids is fluorocarbon 22, which is degradable in the troposphere and is not considered a serious threat to stratospheric ozone.

Fluorocarbon-22

Fluorocarbon-22 is expected to react in the troposphere, yielding chlorine oxide and carbonyl fluoride. The chlorine oxide will be converted to hydrogen chloride in the troposphere and then be removed in precipitation. The carbonyl fluoride might also be removed in precipitation, but even if it is not, the carbonyl fluoride would not decompose stratospheric ozone to any great extent. Thus fluorocarbon-22 may become a candidate for increased use rather than decreased use. The compound is especially useful in refrigeration applications, whose continuation is highly desired. Fluorocarbon-22 should be looked at as a possible substitute for fluorocarbon-11 and fluorocarbon-12, although it will require system redesign. Before a large increase the release of fluorocarbon-22 is permitted, information should be sought on the atmosphere lifetime and the health effects of carbonyl fluoride.

Methyl Chloride

If the belief in an extremely large natural source of methyl chloride persists, it will be difficult to see the need for control of the much smaller amount of methyl chloride emitted as a result of human activities.

Methyl Chloroform

The large volume of methyl chloroform emissions and the long atmospheric lifetime require that the compound be ranked tentatively as a threat to stratospheric ozone. Most emissions of methyl chloroform are a result of metal cleaning operations. These emissions can be reduced by installation of vapor confinement systems, condensers, and other control devices. Where these devices cannot be employed, a shift to alternate solvents would be required.

Methylene Chloride

Methylene chloride (CH_2Cl_2) should be rated as a possible threat to stratospheric ozone, until proven otherwise. This rating is based on the large volume of methylene chloride released, its moderate rate of photo-oxidation, and its production of phosgene, which has an unknown atmospheric behavior. The major releases of methylene chloride occur during its uses as a solvent and as a paint remover. These will be difficult to control. If further study confirms that methylene chloride is carrying a substantial amount of chlorine to the stratosphere, substitute compounds should be sought.

Perchloroethylene

Perchloroethylene emissions are very large but the atmospheric lifetime of the compound is relatively short--probably on the order of a few days. If the parent compound were the only consideration, there would be no need to be concerned with control measures. There are, however, photo-oxidation products to be considered. The main product is trichloroacetyl chloride, and a lesser product is phosgene. If these compounds are found to persist in the troposphere long enough for them to cross into the stratosphere, then perchloreoethylene controls may have to be considered. In dry cleaning applications perchloroethylene losses may be reduced by the use of carbon adsorption units or other devices. The feasibility of such control is shown by the case of fluorocarbon 113, a more expensive dry cleaning agent. Since the economics of control have been favorable for F-113, installations using it have been designed for solvent recovery. The result has been a rate of solvent loss during operation that is only about one-sixth as great as in installations using perchloroethylene.

Trichloroethylene

Trichloroethylene is emitted on a large scale. The compound is photo-oxidized rapidly in the air, its lifetime being on the order of one day. The fate of the oxidation products, dichloroacetyl chloride and phosgene is not yet established, however, and the compound may therefore be considered a candidate for control measures. Much of the trichloroethylene losses occur during metal cleaning operations. These emissions may be controlled by greater use of vapor confinement systems, condensers and similar devices.

Vinyl Chloride

The chlorine in vinyl chloride is not likely to get out of the troposphere. The vinyl chloride will be photo-oxidized within a day of its release, with the formation of hydrogen chloride. This HCl will soon be taken out at surfaces or in precipitation. From the point of view of stratospheric ozone, therefore, there is no need to control vinyl chloride.

SECTION VI
REGULATORY AUTHORITIES OF EPA

As the IMOS study correctly indicated, the nature of the potential fluorocarbon problem is such that any regulatory decision should be made with caution and should be based on supportive scientific and technical data. Yet, by the time the effects become measurable, an adverse impact may have already resulted. Therefore, decisions on regulation require that the significant knowledge gaps concerning the problem be filled within a few years. The fluorocarbon manufacturing industry is already conducting substantial research in the area; the results of these studies, coupled with the results of the work by government agencies, the universities and the National Academy of Sciences should supply the technical information necessary for sound decision-making. The timetable for the decision-making process is in the neighborhood of two years.

In terms of current regulatory authority, fluorocarbons used as propellants in pesticide products can be regulated by EPA under the Federal Insecticide, Fungicide, and Rodenticide Act. EPA also believes that it has existing authority under Clean Air Act section 303, the emergency powers section, to deal to a limited extent with the general release of fluorocarbons to the upper atmosphere. This section would permit an action to enjoin the production or use of fluorocarbons if EPA determines they are presenting an imminent and substantial endangerment to the health of persons. There are difficulties with this approach, however, as it protects only hazards to public health and does not extend to broader environmental endangerment. Furthermore 303 makes the courts the initial triers to facts on the health evidence, and it is possible that a court would be reluctant to ban the production and use of a product unless presented with extremely strong health case.

A better regulatory approach, should one be needed, is the use of a comprehensive and general regulatory mechanism such as the pending Toxic Substances Control Act. Enactment of the Act would address both the public health risks and environmental threats which may be caused by chemical substances including fluorocarbons.

SECTION VII
RESEARCH NEEDS

The mathematical models that predict stratospheric ozone destruction are formulations of the chemical facts determined from experimentation. New data on the atmospheric concentrations of halogenated pollutants and on their chemical reactions will therefore have a direct impact on the predictions. Present and proposed experimental studies within the EPA program will interact with the model predictions in a major way by indicating the total flux of chlorine-containing pollutants into the stratosphere. Obtaining a value for the flux of bromine containing pollutants into the stratosphere might also strongly affect the predictions. If the degree to which the chlorinated carbonyl compounds are penetrating the stratosphere can be established and the details on their photolysis rates and products are outlined, then the photodissociation of these compounds can also be incorporated into the models. The research needs roughly fall into two groups: needs for measurements in the atmosphere, and needs for further laboratory studies.

ATMOSPHERIC MEASUREMENTS

The measurement program should have two aspects: (1) improvement of measurement methods, and (2) application of the methods at all accessible levels of the atmosphere.

While there is a current urgency to the problem of the chlorinated compounds, the measurement program should not be restricted to them. The problem of the supersonic transport exhaust and the problem of the halogenated pollutants both illustrate the need for measurement of a wide range of physical and chemical properties of both the stratosphere and troposphere.

The man-made emissions that might perturb the chemistry of the stratosphere can be classed as direct and indirect. Direct emissions include halogenated compounds released during industrial and domestic use, and nitrogen oxides from high flying aircraft. At present the major uncertainty as to the perturbation of the stratospheric chemistry lies in the lack of knowledge of the degree in which each of the halogenated pollutants is contributing chlorine atoms to the stratosphere.

Indirect emissions include N_2O from the soil and sea above the continental shelves. Farming and other activities may stimulate these otherwise stable natural emissions. Also included in the indirect category may be the emission of methyl chloride by marine algae and during the smoldering combustion of vegetation. Another category of indirect emission is the formation of chlorinated compounds during waste treatment with chlorine.

It is not practical or advisable to separate the chemistry of the halogen atoms from the general chemistry of the stratosphere.

Measurement needs are therefore defined below from the point of view of the entire chemical system in the stratosphere.

Within the family of halogenated compounds, we need to measure both the parent molecules and their decomposition products. Among the parent compounds we include the chlorofluorocarbons CCl_2F_2, CCl_3F, which are unequivocally man made. Compounds wholly or partially natural in origin are CH_3Cl, and CH_3Br. The decomposition products are numerous and important in identifying the significant sources of stratospheric chlorine. This includes HCl, HF, $COCl_2$, COF_2, chlorinated aldehydes, and chlorinated acid chlorides. Compounds which might be important as sinks for chlorine are $HClO_3$, $HClO_4$, and Cl_2O_7. The free radicals ClO and Cl are a major importance in the cycle of catalytic destruction of O_3, and should be measured, if possible.

Nitrogen oxides should be measured. This includes N_2O, NO, NO_2, and N_2O_5. This whole group of compounds is intimately tied into the stratospheric ozone balance. The ozone itself most certainly needs to be monitored with greater precision and accuracy than in the past.

Many components of natural origin in the atmosphere such as CH_4, CO_2 fine particles, and H_2O are important in stratospheric chemistry. These species also should be the object of further efforts at measurement.

Although the concentrations of free electrons and of negative ions may be low in the stratosphere, the reactions of these negative charge carriers with NO_x and halogens are very rapid. In situ measurements of these negatively charged particles would be of great value.

The chemistry of the stratosphere is modified by mixing and mass transfer processes. Especially important are those processes affecting the transfer of air to and from the troposphere and also to and from the regions where high energy UV radiation is abundant. Much more needs to be known about these air motions and their modifications diurnally, seasonally and long term. The experimental program should include the calculation of fluxes and eddy diffusion gathered from the direct measurement of the distribution of tracers of opportunity such as CCl_2F_2, SF_6, and perfluorocarbons.

Concentrations of species should be measured in the three dimensions of altitude, latitude, and time. For example, altitude and latitude variations of halogenated compounds can yield their reaction rates in the atmosphere. Diurnal variations of concentrations give clues to the chemical kinetic mechanisms and rates for the trace species. Sampling of rainwater is important to determine whether or not product species are present as a result of rainout or washout processes.

MEASUREMENT TECHNIQUES

Measurement methods for halogenated pollutants almost all fall into two classes:

(1) Gas chromatographic methods
(2) Optical methods

The gas chromatographic method has laid the foundation of atmospheric

data that has allowed chemists to perceive the threat of chlorine-ozone interactions in the stratosphere. This method will continue to be the primary source of information bearing on the problem. The strength of the method lies in its capability to detect pollutants at concentrations as low as one part pollutant in 10^{11} parts air. Furthermore, this detection sensitivity is achieved in samples that have not been concentrated, using a sample volume of approximately five cubic centimeters. If cold trapping techniques are used, the detection sensitivity is increased further.

Uncertainties in the application of the chromatographic method arise from the possibility of chemical reactions during the passage of the pollutant through the column and from a lack of a distinctive signature by which to identify unknown pollutants. For identification purposes the chromatograph is often coupled to a mass spectrometer or an infrared spectrometer.

Development needs of the chromatographic method lie in the direction of specific identification and absolute calibration. Even without further development, however, the method can yield much of the needed data on halocarbon distribution and reactions. A proper balance of effort on chromatographic work would involve a modest program of development and a heavy program of application of the existing method. There is a particular need for development of techniques of measuring ultra trace quantities of halocarbons in rainwater.

Probably the optimum mode of operation in chromatographic studies is to collect air samples as functions of altitude, latitude, and time, and return them to the laboratory for analysis. In addition to measuring the halocarbon pollutants themselves, efforts should be made to measure the chlorinated aldehydes, acids, and acid chlorides that are the primary products of photooxidation of the halogenated pollutants.

Optical methods have their most important role in the measurement of labile and transitory species in the air, especially those engaged in a sequence of reactions in which the predicted steady state concentrations are sensitive to the choice of rate constants. Acids are lost on vessel walls and therefore should be measured without collection. HCl is important and probably is feasible to measure by spectrometers or interferometers looking at sunlight or moonlight. HF is a key ingredient in the fluorocarbon problem since the ratio of HF/HCl can be predicted if these both arise from the photodissociation. The departure from this ratio could give the relative importance of the fluorocarbons and the other chlorinated compounds in the ozone balance.

$HClO_3$ and $HClO_4$ levels in the stratosphere are key to predicting the course of reaction and the extent of ozone depletion. Recommended measurement techniques include the following:

(1) Spectroscopic analysis of pollutant concentrates. A method of concentrating pollutants from air samples at liquid nitrogen temperature has been developed in this laboratory and is currently being used. This method can measure fluorocarbons and other halogenated pollutants down to mixing

ratios of 1 in 10^{12}. Detection in some important cases, such as methyl chloride, is limited by spectral overlaps. This work should be continued.

(2) Long path absorption spectroscopy through the troposphere. A four kilometer controlled path multiple reflection system is being constructed at Research Triangle Park for this study. Measurements will be carried out in the coming year at Pasadena, California, using an infrared Fourier Transform spectrometer system.

(3) Non-dispersive analysis for selected pollutants. The non-dispersive infrared technique has particular promise for measurement of hydrogen chloride. A system for this purpose is currently under development at Research Triangle Park,.

(4) Solar and lunar spectroscopy of the upper atmosphere. Grating spectrometers, interferometers, non-dispersive analyzers or laser heterodyne spectrometers may be used to measure long path absorption of the solar or lunar radiation.

(5) Long path absorption measurements in the stratosphere with folded cavities or between two balloons. This technique could be specifically applicable to ionic species, unstable free radicals and in general to strongly reactive gaseous species.

LABORATORY STUDIES

The atmospheric chemistry of the halogenated pollutants is still not well enough known to allow reliable predictions of what happens to the pollutants in the real atmosphere. While atmospheric measurements will give many new clues as to the chemical processes, there are still unknown factors that can be determined in the laboratory. These unknown factors can be classed as follows:

(1) Photooxidation mechanisms

(2) Rates of individual oxidation reaction steps

(3) Overall conversion rates for gaseous reactions

(4) Rates of photodissociation of primary pollutants

(5) Rates of photodissociation of secondary pollutants (Reaction products)

(6) Products of photodissociation

(7) Rates of hydrolysis of acid chlorides and phosgene

(8) Fate of hydrolysis products

(9) Uptake of acids and acid chlorides in precipitation

The above list indicates the need for a major laboratory effort on the secondary pollutants. The importance of these reaction products is emphasized by Figures 1 and 2 which illustrate the high proportion of chlorinated pollutants that are not fluorocarbons. It must be remembered especially that the acids, aldehydes, acid chlorides and phosgene are all strong absorbers of ultra violet light. Chlorine will be released from these compounds by photodissociation more readily than it will be released from fluorocarbons.

In addition to the current major chlorinated pollutants, other compounds will undoubtedly come to the fore as usage patterns change and alternates to present compounds are developed. In the program of laboratory studies, due consideration must be given to the atmospheric chemistry of such alternate compounds and their decomposition products.

SECTION VIII
REFERENCES

1. Fluorocarbons and the Environment. Report of Federal Task Force on Inadvertent Modification of the Stratosphere (IMOS). Council on Environmental Quality and Federal Council for Science and Technology (co-sponsors). June 1975. 109 p.

2. Preliminary Economic Impact Assessment of Possible Regulatory Action to Control Atmospheric Emissions of Selected Halocarbons, Draft Report. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, N.C. EPA Contract No. 68-02-1349, Task 8. Prepared by Arthur D. Little, Inc., Cambridge, MA. July 1975.

3. Lovelock, J.E. Atmospheric Fluorine Compounds as Indicators of Air Movements. Nature. 230: 379-380, 1971.

4. Lovelock, J.E., R. J. Maggs, and R. J. Wade. Halogenated Hydrocarbons in and Over the Atlantic. Nature. 241: 194-196, 1973.

5. Rowland, F.S., and M. J. Molina. Chlorofluoromethanes in the Environment. Division of Research, U.S. Atomic Energy Commission. AEC Contract No. AT(04-3)=34, P.A. 126. AEC Report No. 1974-1. Department of Chemistry, University of California, Irvine, CA. September 1974.

6. Singh, H.B., and D. Lillian. Gas Chromatograhic Methods for Ambient Halocarbon Measurements. Submitted for publication in the J. Air Pollu. Contr. Assn.

7. Hanst, P. L., L. Spiller, and D. Watts. Infrared Measurement of Halogenated Pollutants and Other Atmospheric Trace Gases. Submitted for publication in the J. Air. Pollu. Contr. Assn.

8. Relevant reports issued by the Center for Air Environment Studies, The Pennsylvania State University, University Park, PA. and supported by EPA grant no. R800949.

9. Gay, B.W., P.L. Hanst, J.J. Bufalini, and R.C. Noonan, Atmospheric Oxidation of Chlorinated Ethylenes. Submitted for publication on Environ. Sci. Technol.

APPENDIX A. SUMMARY OF EPA RESEARCH PROGRAM ON HALOGENATED AIR POLLUTANTS-AUGUST 1975

1. Title: Determination of Tropospheric Halocarbons by Gas Chromatography and Mass Spectroscopy

Objective: Measure distributions of halogenated compounds in rural areas, urban areas, and over water. Samples will be gathered in the field and returned to the laboratory for analysis by gas chromatography and mass spectroscopy. Such compounds as CCl_4, CH_3I, CH_3Cl, CH_2Cl_2, CH_3CCl_3 will be measured. Insights into the photochemical reactions will be derived from the detected concentrations and spatial distributions.

Progress: A research grant proposal was solicited from Washington State University. The proposal was received and approved by intramural and extramural reviewers. The grant is presently being processed for award.

2. Title: Infrared Analysis for Tropospheric Halogenated Compounds

Objective: Condense a large volume of air in a cold trap and boil off the oxygen and nitrogen. Vaporize the remaining condensate into a long path infrared cell and run the spectrum, using a Fourier Transform Spectrometer. Remove carbon dioxide interference by the ratio technique and measure the infrared bands of the other trace constituents. Trace gases with mixing ratios as low as one in 10^{12} are detectable by this method. Samples will be collected at urban, rural, and maritime locations.

Progress: This task has been carried out on an intramural basis. The pollutants have been condensed and analyzed using a mobile laboratory. Tests were carried out at Research Triangle Park, North Carolina, Atlantic Beach, North Carolina, and New York City. Background levels of Freon 11, Freon 12, Carbon tetrachloride, acetylene, carbonyl sulfide and other compounds have been established. Methyl chloroform and Freon 22 have also been measured, but have been shown not to be ubiquitous as is the case with the fully halogenated compounds. A paper entitled "Infrared Measurement of Halogenated Pollutants and Other Atmospheric Trace Gases," has been submitted to Journal of the Air Pollution Control Association.

3. Title: Atmospheric Measurements to Determine Fates of Halogenated Compounds

Objective: Study the tropospheric distributions and chemical behavior of halocarbons. Direct atmospheric analysis will be carried out using the gas chromatographic method with electron capture detection and absolute coulometric calibration. Measurements will be made on urban air, maritime air, and inland air in a rural area.

Progress: A research grant has been awarded to the Stanford Research Institute. A mobile laboratory is being prepared for measurements at Los Angeles, Point Reyes, California, and the Coachella Valley.

4. Title: Atmospheric Analysis Over a Four Kilometer Optical Path

Objective: Record the infrared absorption spectrum of the atmosphere in an urban area, using an optical path long enough to bring out the weak bands of halocarbons, halogenated acids, phosgene, and related compounds. This task is directed towards understanding the photochemistry of urban air, including in addition to the halogenated compounds, the hydrocarbons, oxidants, nitrogenous compounds, and sulfur compounds.

Progress: This is an intramural task, with contractor support. A multiple-reflection optical system is being constructed for use with a Fourier Transform Spectrometer. Eight mirrors will be mounted, four at each end, in an optical tunnel 25 meters long. The system will be operated on the roof of the Keck Engineering Building at the California Institute of Technology, Pasadena. The body of the absorption cell is under construction. The cell will be installed at Research Triangle Park for preliminary testing before it is moved to Pasadena. Mirrors will be delivered this month.

5. Title: Tropospheric Photochemistry of Halogenated Compounds - Laboratory Studies

Objective: Rates of photooxidation of halogenated compounds will be determined under simulated tropospheric conditions. Rates of disappearance of reactants will be determined; products will be identified, and reaction mechanisms will be derived.

Progress: A research grant was awarded to the Ohio State University

in July. A long path photochemical reactor of unique design that has been constructed at the Ohio State University will be used in these studies. A government owned Fourier Transform Spectrometer will be used to monitor the progress of the chemical transformations.

6. Title: Chemistry of Degradation of Halogenated Compounds in the Atmosphere

Objective: The chemical mechanisms of degradation of the halogenated pollutants will be determined in laboratory measurements. Photooxidations will be carried out under simulated atmospheric conditions in a laboratory reaction chamber that permits observation of the consumption of reactants and the formation of products. Indications of stratospheric effects will be derived from the observed reaction products and rates.

Progress: This task is being carried out on an intramural basis, complementary to the Ohio State Research Grant.

Five chlorinated ethylenes, along with chloroform, Freon 22, methyl chloroform, and methyl chloride have been studied in a long path infrared cell and photochemical reactor. Identified products include monochloro, dichloro, and trichloro acetyl chlorides, phosgene, chlorinated peroxy acetyl nitrates, carbonyl chloro fluoride, trichloro acetaldehyde, formyl chloride, and hydrogen chloride. Many of these products have ultraviolet absorption characteristics that could lead to chlorine deposition in the stratosphere. A publication entitled "Atmospheric Oxidation of Chlorinated Ethylenes," has been submitted to Environmental Science and Technology.

7. Title: Halocarbon Reactions in the Atmosphere

Objective: Through laboratory experiments determine rates of degradation of halocarbon pollutants in the troposphere and stratosphere. Determine the lifetimes and the eventual fate of the intermediate products of the photooxidation.

Progress: A research grant was awarded to the Illinois Institute of Technology Research Institute (IITRI) in July. A grant review was held in Chicago on July 30. The IITRI group will concentrate on (1) measuring the rate of OH attack on halocarbons, and (2) measuring photolysis rates, quantum yields, and products in the direct photo-dissociation of the acyl chlorides, phosgene, and other compounds produced in the photooxidation of the chlorocarbons.

8. Title: Hydrogen Chloride in the Troposphere

Objective: The abundance and distribution of hydrogen chloride will be determined in both urban and rural regions. From the measurements, inferences will be drawn as to the sources and sinks of HCl. Removal rates will be determined. The measurement technique will be line-reversal infrared correlation spectroscopy which will be capable of measuring HCl partial pressures as low as 10^{-10} Atm.

Progress: This is an intramural task being carried out with contractor support. The transmitter for the non-dispersive analyzer for hydrogen chloride has been constructed, and operated successfully. Its operation will be tested over a 500 meter folded path in the laboratory.

APPENDIX B. PRELIMINARY ASSESSMENT OF ECONOMIC IMPACT OF ALTERNATIVES TO CONTROL FLUOROCARBON EMISSIONS TO THE ATMOSPHERE

INTRODUCTION

The purpose of this appendix to the report is to provide a preliminary assessment of the alternatives for emission abatement and the potential economic impact of possible regulatory controls for selected fluorocarbons. In particular, this assessment will focus on those compounds which are produced in large volumes, namely fluorocarbons 11, 12, and 22.

This section will first identify the end use areas of these compounds where emissions to the atmosphere are the greatest. Then, with these areas identified, the potential solutions for controlling or eliminating the emissions will be assessed. One solution that will be considered is an outright ban of the compounds which will necessitate a switch to alternative products, processes, or chemicals. These alternatives will be considered both in terms of product performance and their current or future availability. Other solutions for controlling emissions other than a total ban, such as containment and recovery of the emissions, will also be identified.

Regulatory control strategies for possible emission control alternatives will be outlined and the possible economic impact associated with each will be assessed. The intention of this qualitative economic impact analysis is to identify industry sectors that may be severely impacted by possible regulatory action. Because of severe time constraints in the original study, this analysis does not attempt to quantify the impacts.

The information presented in this appendix of the report is taken from an extensive report entitled "Preliminary Economic Impact Assessment of Possible Regulatory Action to Control Atmospheric Emissions of Selected Halocarbons," which was prepared by Arthur D. Little, Inc. for EPA.

EMISSION PROBLEM AREAS

Fluorocarbons

For the fluorocarbons of interest (F-11, F-12, F-22), the emissions from production, transport, and storage are small (about one percent), thus most of the emissions come from the end-use areas (see Table B-1). As shown, the largest source of emissions are aerosol sprays, which contributed 486 million pounds in 1973, or about 66% of the total U.S. emissions of F-11, F-12, and F-22. Essentially all of these emissions were F-11 and F-12 since only an insignificant amount of F-22 is used in aerosol applications. There is little timed release of these compounds in the propellant applications since they are lost for the most part within six months of production.

The next largest source of emissions are refrigeration and air conditioning systems, where the fluorocarbons are used as refrigerants. The emissions from these applications amounted to roughly 201 million pounds in 1973, or 27% of the total fluorocarbon emissions (Table B-1). Of these refrigerant emissions, about two-thirds were F-12 and more than one-quarter were F-22 while only a small amount were F-11. The fluorocarbon emissions from refrigeration systems are not immediate but are instead phased over the life of the system. Therefore, the emissions in 1973 were actually fluorocarbons that were produced in past years, as far back as 15 years or so.

Thus, the propellant and refrigerant applications are the sources of nearly 94% of the emissions of the three fluorocarbons of interest. Since the use of these compounds in the other end-use categories is relatively minor, the emissions are comparatively small. Blowing agent applications of fluorocarbons contributed nearly 37 million pounds (mostly F-11) in 1973, while emissions from solvent and plastic resin usage were negligible.

Table B-2 breaks down the F-11 and F-12 emissions from propellant applications by aerosol type. Over 80% (by weight) of these compounds as propellants are used in personal aerosol products, so as expected this is the prime emission problem area. For the year 1973 nearly 84% of the emissions of F-11 and F-12 from propellant applications, or 408 million pounds, came from personal products. Of the overall propellant total, over 77%, or 375 million pounds of the emissions came from hair care products and antiperspirants and deodorants.

Use of fluorocarbons as refrigerants is predominantly in air-conditioning applications, which account for over 85% of annual F-11, F-12, and F-22 consumption in this end-use category. Thus, it follows that most of the refrigerant emissions of fluorocarbons come from air conditioning systems, as Table B-3 indicates. By far the largest emission source is mobile (mainly automobile) air-conditioning, which contributed 71 million pounds or 35% of the total fluorocarbon refrigerant emissions. The other primary emissions problem areas are: food store refrigeration of refrigerant emissions), commercial unitary air-conditioning (12.5%), residential unitary air-conditioning (8.8%), and large centrifugal chillers (7.7%).

In conclusion, over 74% of the total annual emissions of F-11, F-12, and F-22 originate from antiperspirants and deodorants (27%), hair sprays (22%), and mobile air-conditioners, (10%).

ALTERNATIVES FOR EMISSION ABATEMENT

Aerosol Propellants

The fluorocarbons are one of three major types of propellants used in aerosol products today. The other two are compressed gases and hydrocarbons, the latter of which are liquified gas propellants like the fluorocarbons. Even though they are significantly more expensive than other propellants, fluorocarbons have gained widespread use in personal products because they offer an advantageous combination of properties. These include:

Table B-1. ESTIMATED U. S. FLUOROCARBON EMISSION - 1973
(Millions of Pounds)

Fluorocarbon	Production, transport and storage emissions		Annual emissions from use and disposal						
	Production (million lbs)	Emissions[a] (1 percent)	Propellant	Refrigerant	Solvent	Blowing Agent	Plastic Resin	Total[b]	Percent of Total
F-11	334	3.3	236.9	11	sm.	29.3	-	280.5	38.2
F-12	489	4.9	249.4	130.5	-	7.5	-	392.3	53.5
F-22	136	1.4	sm.	59.5	-	-	sm.	60.9	8.3
Total[b]	959	9.6	486.3	201.0	sm.	36.8	sm.	733.7	
Percent of total		1.3	66.3	27.4	-	5.0	-		100.0

Sm. = less than 5 million pounds; - = none or negligible

[a]Emissions from production transport and storage are judged to be approximately 1 percent of total production

[b]Does not include 'sm.'

Source: Arthur D. Little, Inc., estimates, based on industry contacts

Table B-2. ESTIMATED U.S. FLUOROCARBON EMISSIONS AS AEROSOL PROPELLANT[a] BY PRODUCT TYPE - 1973

Aerosol Type	Aerosol Unit Estimates[a]				Fluorocarbon Propellant Emissions Estimates (millions of pounds)				
	Millions of Units Filled	Percent of Units Propelled by F.C.	Average Weight (lb/unit)	Average Percent Propellant Per Unit		F-11 Emissions	F-12 Emissions	Total Emissions	Percent of Total
Personal									
Hair Care	469	90	0.8	50	Subto	103.0	72.0	175.0	36.0
Antiperspirants and deodorants	577	100	0.6	65		85.5	114.3	199.8	41.1
					Subtotal	188.5	186.3	374.8	77.1
Medicinal and Pharmaceutical	66	90	0.4	80		11.0	5.5	16.5	3.4
Colognes and Perfumes	144	100	0.1	45		-	1.0	1.0	0.2
Shave Lathers	171	10	0.6	10		-	0.4	0.4	0.1
Others	70	90	0.5	60		7.5	7.5	15.0	3.1
Household					Subtotal	18.5	14.4	32.9	6.8
					Subtotal	207.0	200.7	407.7	83.9
Room Deodorants	170	30	0.5	50		2.7	5.0	7.7	1.6
Cleaners	211	10	0.9	20		2.1	2.1	4.2	0.9
Laundry Products	163	50	0.9	35		4.2	6.0	10.2	2.1
Waxes and Polishes	105	30	0.8	15		1.5	2.5	4.0	0.8
Others	43	30	0.8	50		2.0	2.0	4.0	0.8
All other Products					Subtotal	12.5	17.6	30.1	6.2
Insecticides	143	30	0.9	40		5.5	9.0	14.5	3.0
Coatings	268	10	0.8	45		3.4	6.6	10.0	2.1
Industrial	132	50	0.9	50		6.0	11.0	17.0	3.5
Foods and Pan Spray*	115	15	0.8	65		-	-	0.0	0.0
Automotive	89	30	0.8	30		1.0	2.5	3.5	0.7
Vet. and Pet	16	50	0.5	50		0.5	0.5	1.0	0.2
Others	34	50	0.6	30		1.0	1.5	2.5	0.5
Total Units Filled	2,986				Subtotal	17.4	31.1	48.5	10.0
Total Emissions (Millions of pounds)						236.9	249.4	486.3	100.0
Percent of Propellant Emissions						48.7	51.3	100.00	

[a] Use and filling emissions for products produced in 1973; emission lag averages 6 months for most products; some unit estimates rounded

Sources: Chemical Specialties Manufacturers Association and Arthur D. Little, Inc. estimates

* Propelled by F-114

Table B-3. ESTIMATED U. S. FLUOROCARBON REFRIGERANT EMISSIONS - 1973
(millions of pounds)

Type of Equipment	Refrigerant Commonly Used	Emissions	Percent
Major Appliances			
Room A/C	22	7.6	3.8
Dehumidifiers	12	0.2	0.1
Freezers	12	1.7	0.8
Refrigerators	12	2.9	1.4
Other			
Ice Makers	12	0.1	0.1
Water Coolers	12	0.2	0.1
Mobile A/C	12	70.9	35.3
Unitary Residential A/C	22	17.6	8.8
Unitary Commercial A/C	22	25.1	12.5
Centrifugal Chillers	11,12,22	15.5	7.7
Reciprocal Chillers	11,12,22	7.2	3.6
Unit Coolers	12	1.8	0.9
Food Store Refrigeration	12,22	26.2	13.0
Mobile Refrigeration	12	1.2	0.6
Beverage Refrigeration	12	4.6	2.3
Packaged Terminal A/C	22	0.2	0.1
Other	--	18.0	9.0
TOTAL		201.0	100.0

SOURCE: Arthur D. Little, Inc. "Preliminary Economic Impact Assessment of Possible Regulatory Action to Control Atmospheric Emissions of Selected Halocarbons."

- Safety - essentially non-toxic and nonflammable

- Liquified gas form - provide relatively uniform pressure over the life of the product and aid in producing a fine (true aerosol) spray

- Versatility - fluorocarbons can be blended to provide a range of press and solubility characteristics

- Chemical Stability/Inertness - little or no deleterious effect on other components of product formulation or on the container

- Odorless - especially important for perfume formulations

In the event of a possible ban on the use of fluorocarbons in aerosol sprays, which is the only conceivable method to control emissions, the producers and marketers of aerosols would have to switch to substitute products which, while not performing as well overall as fluorocarbons, would nonetheless perform satisfactorily in most cases. These substitutes would be:

- liquid gas propellants,

- compressed gas propellants,

- mechanical pump systems, or

- non-spray products,

However, to make a direct subsitution of one type of propellant for another or subsitute a mechanical delivery system for an aerosol system without significantly altering the characteristics of the product in question is generally conceded to be impossible. Reformulation of existing products would be necessary since fluorocarbons are an essential part of the present formulations.

Because of their higher cost, fluorocarbons are used sparingly in aerosol products other than personal products. Most household and other products exist satisfactorily with hydrocarbon or compressed gas propellants because the safety or product performance problems are not as critical. For example, flammability is not a problem in water-based products while a true aerosol spray is not important in most applications other than personal products.

In personal product applications substitutes for fluorocarbons exist, although these alternatives may not have all the desirable qualities of fluorocarbons. However, a definitive statement cannot be made as to whether these products perform effectively enough because consumer preferences are so varied. These products may perform well enough for many people, while for others they may be totally inadequate.

Hydrocarbons used as liquified gas propellants include isobutane, propane, n-butane, and dimethyl ether, with the first two being the most widely used. Hydrocarbons offer most of the performance features of fluorocarbons and are appreciably lower in cost. However, they are highly flammable which has prevented their general use as substitutes for fluoro-

carbons in personal products. In order to combat this problem, methylene chloride and methyl chloroform have been used as vapor depressants so as to suppress the inherent flammability of the hydrocarbons. Indeed, the combination of hydrocarbons and methylene chloride in both hair sprays and dry-type antiperspirants have been marketed to a limited extent for several years. Methylene chloride apparently causes skin irritation, but some industry representatives contend this problem can be avoided by correct formulation. However, the status of both methylene chloride and methyl chloroform with relation to the ozone layer is uncertain at this time.

Compressed gas propellants, such as nitrogen, carbon dioxide, and nitrous oxide, are low in cost, nonflammable, and exhibit low toxicity. In most cases the propellants can readily substitute for fluorocarbons, especially in non-personal products. However, their drawback is that they have undesirable pressure characteristics that typically cause a coarser spray, which is unsatisfactory in most personal products. In this regard, considerable work has been conducted in developing improved special valves to accommodate carbon dioxide characteristics that markedly improve spray quality to the point that they are said to be entirely satisfactory for hair sprays and other personal products. At least one carbon dioxide based hair spray is currently undergoing limited market testing, according to some sources.

Many mechanical devices and other delivery systems provide potential alternatives to the fluorocarbon propelled aerosols. Finger- or hand-activated mechanical pumps represent an area of considerable interest and development effort. A pump-based hair spray was brought on the market in 1972, and at least seven companies now offer both men's and women's hair sprays that use pump delivery systems. Because of changing hairstyles, desire for different hair feel and other considerations, these products have performed much better than expected and the companies are having difficulty meeting demand. The current demand level is on the order of 50 to 60 million pumps per year for hair care products. This is approximately 13% of the number of aerosol hair care units marketed in 1974.

Nearly all antiperspirants and deodorants currently exist in non-spray form in addition to the aerosol form. These are in the form of squeeze bottles, roll-on applicators, stick-type applicators, squeeze tubes, wick-type dispensers, saturated pad applicators, felt tip applicators, and other products which can be applied by hand from a glass or plastic container. These products have existed for years and still gain widespread use.

While all these alternatives to fluorocarbons have already undergone extensive development, none presently exist in sufficient quantities to satisfy the consumer demand. Of the possible alternatives, the mechanical pump systems and the non-spray products appear to be most readily available. It is estimated, however, that incremental capacity expansions could take place within a relatively short time (one to two years) that would allow production in sufficient quantities to meet demand.

While the technology for compressed gas aerosols exists, testing of the acceptance of their different performance characteristics by consumers is now only beginning. Up to three years are likely before these products can meet a significant portion of the demand. Provided

the skin irritation and possible environmental problems associated with methylene chloride in personal products are overcome, hydrocarbon-based aerosols likely will be available within two years to satisfy a portion of the consumer demand.

In summation, in the event of a ban on the use of fluorocarbons in aerosol sprays, aerosol marketers likely would first expand the production of their non-aerosol products and in parallel refine and further develop existing liquified gas propellants and compressed gas propellants. Work would also begin on developing new liquified gas propellants, but these probably would not be available for several years since no new propellants have been identified.

Refrigerants

Fluorocarbons have become the basis for our domestic air conditioning and refrigeration industry. Presently 92% of all refrigerants used in the dominant vapor compression cycle are either F-11, F-12, or F-22 with F-12 representing about 56% of the market and F-22 making up about 30%. The safe properties of these products have permitted their use under conditions where flammable and more toxic refrigerants would be hazardous to use.

In order to control or eliminate emissions of fluorocarbon refrigerants, four potential solutions exist, some more viable than others:

- Use of alternative refrigeration systems
- Use of alternative refrigerants
- Leak prevention and recovery of refrigerant during servicing or disposal
- Reduction or elimination of refrigeration and air conditioning

Most would agree that the last alternative would have extensive and drastic ramifications on the U.S. society. Our current food distribution and storage network is critically dependent on refrigeration. While air-conditioning may be a luxury item in some cases, it is almost essential in hotter climates and in modern buildings that were constructed without opening windows and thus are dependent on air conditioning systems.

Alternative refrigerants in the vapor compression cycle exist, but their current use is extremely limited because fluorocarbons have proven to be inherently safer and better refrigerants. Furthermore, these alternatives cannot be substituted directly in existing systems. Instead, such substitution would involve total and major redesign of refrigeration systems.

Ammonia is one of the best refrigerants known today from a standpoint of system performance because of its attractive physical properties. However, it is both toxic and flammable; hence its use has been restricted to industrial food storage and manufacturing operations where the enforcement of safety practices and precautions is feasible. For use in commercial buildings and in homes, a major redesign would be required to contain the ammonia cycle equipment out-of-doors where chances of hazards would be minimized.

Hydrocarbons are good performers as refrigerants and are used in industrial environments to some degree. But these compounds, though not toxic, are highly flammable and would thus require adequate safegards against explosive limits in air mixtures.

In the event F-12 is proven to cause destruction of the ozone layer while F-22 is not, then possibly the best substitute refrigerant for F-12 would be F-22. The latter is already well established as a refrigerant in home air-conditioning units, unitary air-conditioning systems, and in central air-conditioning and chillers. In all other refrigerant applications, though, F-22 is not used. Thus, conversion to F-22 would still constitute a substantial redesign task for the industry. Yet, this is not believed to be nearly as significant as with other alternative refrigerants. Nevertheless, the important consideration is that the technology is well established for use of F-22 in many refrigeration systems. However, F-22 likely will not be acceptable for use in auto air-conditioning systems because exposure to high temperatures under the hood would probably cause stability problems for the refrigerant. Whether this problem can be satisfactorily overcome is not known.

Although the vapor compression cycle dominates the refrigeration and air-conditioning industry, other cycles are used. The absorption refrigeration cycle is a well established system and is the most commonly used of these other cycles in home appliances. The ammonia-water cycle has been used in home refrigerators while the water-lithium bromide system is limited to refrigeration above 32^{o}F since the refrigerant freezes at that temperarure. As a result, the latter has been applied principally to commercial air-conditioning. However, under promotional support by the gas industry, even home air-conditioning systems using the absorption cycle have been made and sold in the past. The number of absorption units peaked at 3,193 sold in 1970 and declined to 2,222 in 1973.

There are several drawbacks to the absorption system that could possibly place severe constraints on its immediate use. First, because of the toxicity and flammability of ammonia, this system has not gained general acceptance. Secondly, these absorption systems have very low energy efficiency, which is critical in light of the current energy situation. Furthermore, most unitary absorption equipment and all domestic absorption refrigerators manufactured in the past have used natural or liquified petroleum gas as an energy source, both of which are critically short at this time. Also, because of its extensive heat transfer and surface area requirements, the absorption cycle does not appear to be suitable for automobile air-conditioning. Lastly, while the technology for constructing absorption units is fairly well established, only a few manufacturers have ever made such equipment. Because of this limited production capacity, the industry could not switch to absorption units before three to five years.

Alternative refrigeration systems available for use in automobile air-conditioning appear to be severely limited. As mentioned previously, neither the F-22-based vapor compression cycle nor the absorption cycle hold considerable promise. One potential substitute system is the Brayton cycle which uses a cheap, nontoxic, and safe refrigerant: air.

This cycle, which is used for air-conditioning in some aircraft, offers low weight and compactness over vapor compression cycle equipment, but it has a much higher power requirement that has restricted its use severely and thus makes it relatively impractical for use in automobiles.

If a relatively low level of fluorocarbon emissions can be tolerated, an alternative to changing to new refrigerants or systems is the containment and recovery of a significant portion of the losses to the atmosphere. Theoretically most systems are constructed so that leakage of the refrigerant is minimal. However, because no satisfactory incentives exist to encourage prevention of leaks in the systems, methods have not been practiced by which leaks can be minimized. In addition, no incentives presently exist that encourage recovery of the refrigerant during servicing or disposal. In most cases home refrigeration and air-conditioning units are discarded without recovering the refrigerant. In rechargeable units the original charge is vented to the atmosphere during servicing without being recaptured. This latter practice is believed to be the cause of the bulk of the losses from large stationary systems.

As Table B-4 indicates, about 85% of the annual emissions of fluorocarbon refrigerants are estimated to be potentially preventable through proper design, servicing, and disposal. Manufacturers admit that equipment can be designed and manufactured to meet tighter leakage specifications at an added cost to the consumer, and likewise refrigerant recovery techniques can be utilized in most cases. But currently it is not known what engineering practices will be required to achieve a significant reduction in refrigerant emissions or how much of the emissions can in actual practice be prevented or recovered. Compared to a total redesign of existing systems or a switch to new systems, however, the task of preventing leaks and ensuring proper disposal appears to be considerably easier and less disruptive to the industry.

Thus, given the very high development costs associated with new refrigerants or systems, the extended development time requirements, and large in-service inventory of existing equipment, the containment and recovery of a significant amount of the fluorocarbon emissions appears to be the most cost-effective, short-term method of all the potential solutions discussed, should some level of fluorocarbon emissions still be acceptable from air conditioning and refrigeration systems.

Blowing Agents

Fluorocarbons 11 and 12 are used in the manufacture of foams made from polyurethane, polystyrene, and polyolefins. They are used primarily as the blowing agent which forms the cellular structure. The use of these compounds in polyolefin foam manufacture is quite small in comparison to their use in polyurethane and polystyrene foams. F-11 and F-12 are both safe to use as blowing agents and give the foams excellent insulating properties.

For rigid polyurethane foams, satisfactory substitutes have not been found for fluorocarbon blowing agents that will produce a foam of adequate

Table B-4. ESTIMATED U.S. FLUOROCARBON EMISSIONS AND USE AS REFRIGERANT -1973

Type of Equipment	Refrigerant Commonly Used	Unit Data Existing Units in Service (Millions)	Average Charge (lb/Unit)	Leakage Not Recoveragle (Million lb/yr)	Preventable at Service and with Proper Design[a] (Million lb/yr)	Refrigerant Recoveragle After Disposal (Million lb/yr)	Total Emissions (million lb/yr)
Major Appliances							
Room A/C	22	29.0	2.00	1.2	Small	6.4	7.6
Dehumidifiers	12	5.1	0.84	0.1	Small	0.1	0.2
Freezers	12	22.4	1.25	0.6	Small	1.1	1.7
Refrigerators	12	68.7	0.63	0.9	Small	2.0	2.9
Other							
Ice Makers	12	1.3	2.0	0.05	Small	0.04	0.2
Water Coolers	12	3.8	1.0	0.1	Small	0.1	0.2
Mobile A/C	12	45.0	3.8	6.8	42.8	21.3	70.9
Unitary Residential A/C	22	11.4	9.2	2.1	12.6	2.9	17.6
Unitary Commercial A/C	22	4.0	36.0	2.9	17.3	4.9	25.1
Centrifugal Chillers	11,12,22	0.05	2500	6.3	15.0	2.0	23.3
Reciprocating Chillers	11,12,22	0.2	350	1.4	8.4	0.8	10.6
Unit Coolers	12	1.7	14.0	0.5	Small	1.3	1.8
Food Store Refrig.	12,22	0.2	675	6.8	16.2	3.2	26.2
Mobile Refrig.	12	0.5	14.0	0.1	0.8	0.3	1.2
Beverage Refrig.	12	23.8	1.2	0.6	3.4	0.6	4.6
Packaged Terminal A/C	22	1.0	2.5	0.1	Small	0.1	0.2
Other	-	-	-	2.2	11.9	3.9	18.0
TOTAL	-	-	-	32.8	128.4	51.1	212.3
PERCENT				15.4%	60.5%	21.4%	100%

Small = less than 0.1 million pounds

[a]Preventable through relatively minor modifications to current equipment design or service procedures

Source: Arthur D. Little, Inc., "Preliminary Economic Impact Assessment of Possible Regulatory Action to Control Atmospheric Emissions of Selected Halocarbons"

structural and thermal properties. In the manufacture of flexible polyurethanes, water/carbon dioxide is the primary blowing agent while there are several agents that are used as the necessary auxiliary blowing agent. F-11 is the most common of these auxiliary blowing agents, but methylene chloride is also used and could replace most of the F-11 use.

Hydrocarbons were traditionally used as the blowing agents for extruded polystyrene foams, but because of flammability problems they have been replaced by halocarbons, typically F-12 and methyl chloride. On the other hand, for expanded polystyrene foams, the major blowing agents are pentane and isopentane while F-11 and F-12 are used to a minor extent. For polyolefin foams, other hydrocarbons can readily take the place of F-12.

Instead of restricting the use of F-11 and F-12 as blowing agents, opportunities exist for recovery of fluorocarbons from the manufacture of the foams. For example, the majority (approximately 90%) of the fluorocarbon blowing agent emissions come from the foam manufacturing step. While certain technical problems will have to be overcome, a significant portion of the emissions can have the potential to be recovered by the installation of vapor-recovery equipment.

ECONOMIC IMPACT OF POSSIBLE REGULATORY CONTROLS

Introduction

This section of the appendix attempts to qualitatively assess the economic impact of various alternatives to control the emissions of fluorocarbons. The economic dislocations that are likely to be experienced are identified along with the relative magnitude of the impacts. Quantification of the economic impact, such as projected price increases, job losses or other impacts, is not attempted. Likewise, secondary or tertiary impacts are not considered. This impact assessment only identifies those sectors of the affected industries that have the potential to be impacted so that further study might be directed to them.

There are, however, some general comments which can be made about the economic effects of restricting the use of the fluorocarbons. Because the current uses of the chemicals exist in price and performance competitive environments, one can generally say that for a given product performance the current use of chemical is the best product for satisfying the demand. Restrictions on their use would require present consumers to shift to their next best alternativewhich would either be more expensive or perform less satisfactorily. If these alternatives did not perform satisfactorily enough, then consumers would likely discontinue use and consumption would be reduced. Whether a shift to these alternatives would result in higher priced products is difficult to say. In many cases this may be true, but in aerosol applications for example, the consumer is likely to shift to less expensive products that may perform somewhat less satisfactorily.

Table B-5 provides a summary characterization of the industry sectors that are related to fluorocarbon production and use. The directly-

Table B-5. ESTIMATED EMPLOYMENT AND PRODUCTION VALUE RELATED TO FLUOROCARBON PRODUCTION AND CONSUMPTION - 1973

	Total industry employment	Directly[d] related employment	Total industry production value (1973) 10^6	Directly related production value (1973) 10^6
Raw materials:				
Chlorine[a]	10,300	980	490	45
Hydrofluoric acid[a]	800	330	140	55
Basic chemical production:				
Fluorocarbons	2,700	2,700	240	240
Aerosols:				
Containers	68,200[b]	2,500	4,900	190
Valves, caps & related materials	NA[c]	2,000	NA[c]	60
Concentrate ingredients	NA	NA	NA	NA
Aerosol fillers[e]	14,000	7,000	250	130
Aerosol marketers[e] (total)	15,000	7,500	2,000	1,000
Production	6,000	3,000	--	--
Support (R&D, marketing,) etc.)	9,000	4,500	--	--
Refrigeration: (1972)				
Refrigeration equipment	120,000	120,000	5,600	5,600
Household refrigerators & freezers	32,000	32,000	1,600	1,600
Blowing agent applications:				
Foam products	45,000	30,000	1,000	600
Raw materials	10,000	5,000	460	230

a. "Directly-related" values pro-rated on percentage of total chlorine and hydrofluoric acid demand utilized in the production of the raw materials for fluorocarbons

b. Includes only cans, which represent 95 percent of total aerosol containers

c. NA is not available

d. Related employment refers to production of F-11, F-12, and F-22

e. Directly related employment and production of aerosol fillers and marketers was estimated as 50 percent of total industry employment and production

Source: Arthur D. Little, Inc., estimates

related employment values should not be regarded as an estimate of the jobs to be lost if the production of the chemicals is ended or reduced. While the potential for job losses arises, simply counting jobs may not adequately reflect disruptions resulting from the restrictions because the additional production of alternative products minimizes the employment impact. For example, a ban of fluorocarbon production could result in an increase in the total number of jobs associated with producing the substitute products and performing the function now performed by the fluorocarbons. Thus, while the restrictions on the use of these compounds will have an impact on jobs, it cannot be said with any certainty at this time whether these impacts will be job losses, job gains, or simply having the workers learn to work with new products or chemicals.

Possible Regulatory Options

In order to have a framework within which to assess the potential economic impact, nine possible regulatory options have been defined which are designed to reduce fluorocarbon emissions to the atmosphere by nine different amounts on three different time schedules. Since Federal authority does not presently exist to control the wide range of use of these compounds, these regulatory strategies have no official standing. They are only intended to identify a range of alternatives and to enable a more specific discussion of potential disruptions in the U.S. economy resulting from the options. Other regulatory options are possible and will certainly be considered if a decision is made to restrict the emissions of fluorocarbons.

The options discussed here and the resulting scenarios begin at the point the decision is made. If delays occur before a decision is made, the affected industry sectors will have more time to prepare their response and the resulting economic disruptions could be lessened. The following nine regulatory approaches have been considered:

Immediate (6 months) Restrictions

a. Ban All Uses of Controlled Chemicals After Six Months

All uses (except limited critical uses) of the controlled chemicals would be banned six months after the issuance of the order.

b. Regulate Non-Propellant Uses and Ban Propellant Uses After Six Months

Design specifications would be promulgated requiring the upgrading of refrigeration/air conditioning, and solvent and blowing agent equipment and refrigeration/air conditioning service techniques in order to increase recovery of emissions now lost to the atmosphere. Use in propellant applications (except limited critical uses) would be banned at the end of six months.

c. Do Not Regulate Non-Propellant Uses and Ban Propellant Uses After Six Months

No new controls would be placed on non-propellant uses of the chemicals, but their use as propellants (except limited critical uses) would be banned at the end of six months.

d. Institute Government Control of Total Chemical Production After Six Months

The Federal Government would take some action to limit total chemical production to some tolerable level by the end of six months and let the market mechanisms allocate its uses. The limited production would go to those uses that could afford the resulting significant price increase.

Restrictions After Three Years

e. Ban All Uses of Controlled Chemicals After Three Years

This is the same as Option 1 except that the ban goes into effect at the end of three years.

f. Regulate Non-Propellant Uses and Ban Propellant Uses After Three Years

The regulatory action is the same as Option 2 except that the restrictions go into effect at the end of three years.

g. Do Not Regulate Non-Propellant Uses and Ban Propellant Uses After Three Years

The only restrictions would be a ban of propellant applications three years after the regulation is issued.

h. Institute Government Control of Total Chemical Production After Three Years

After three years total chemical production would be limited to some tolerable level and the market mechanisms would allocate its uses.

i. Do Not Regulate Non-Propellant Applications and Ban Propellant Uses After Six Years

The only controls under this option would be a ban on propellant applications six years after promulgation of the order.

Identification of Economic Impacts

The objective of this section is to identify those industry sectors likely to be impacted by the regulatory options outlined previously and to assess the relative magnitude of the impact. Table B-6 summarizes the results of the economic impact assessment. An estimate has been made of the impact resulting from the 18 regulatory alternatives on 11 primary impact industry sectors.

As a tool for categorizing the magnitude of economic impact, five levels of impact were defined:

a. Severe Impact

A Severe Impact implies that most companies in the sector will be

Table B-6. SUMMARY OF ESTIMATED ECONOMIC IMPACT ASSESSMENT RESULTING FROM RESTRICTION ON U.S. USE OF F-11, F-12, AND F-22

		Impact Sectors							
				Propellant applications			Non-propellant applications		
		Basic chemical producers	Independent fillers	Aerosol industry Can manufacture	Value manufacture	Aerosol marketers	Air conditioning and refrigeration manufacturers		Plastic foam producers
Regulatory options	Emission reduction[1]						F-11, F-12 and F-22 regulated	Only F-11, F-12 regulated	
a.	92%	2-3	1	3	1	2	1	1	2
b.	82%	3	1	3	1	2	4	4	3
c.	70%	3	1	3	1	2	5	5	4
d.	80%	3	1	3	1	2	5	4	3-4
e.	83%	3	2-3	5	2-3	3	1	1-2	3
f.	74%	3	2-3	5	2-3	3	4	4	3
g.	63%	3	2-3	5	2-3	3	5	5	4
h.	69%	3	2-3	5	2-3	3	5	5	4
i.	54%	5	3-5	5	3-5	5	5	5	4

REGULATORY OPTIONS

a. Ban all uses of controlled chemicals after six months
b. Regulation of non-propellant uses and ban of propellant uses after six months
c. No regulation of non-propellant uses and ban of propellant uses after six months
d. Government control of total chemical production after six months
e. Ban all uses of controlled chemicals after three years
f. Regulation of non-propellant uses and ban of propellant uses after three years
g. No regulation of non-propellant uses and a ban of propellant uses after three years
h. Government control of total chemical production after three years
i. No regulation of non-propellant applications and ban of propellant uses after six years

IMPACT CODE

1 - severe
2 - substantial
3 - moderate
4 - limited
5 - none

[1] Percent reduction in U.S. F-11 and F-12 emissions to the atmosphere over a 20 year period beginning in 1976. A 5 percent demand growth per year is assumed in the absence of controls, no restriction on critical propellant uses (5 percent of total), every 5 years one-half of refrigerant in the system at the time escapes, and 50 percent control of emissions from plastic foams are assumed.

affected, at least to a moderate degree (some seriously), and more than 40 percent of the production in the sector related to the controlled chemicals will be ended or significantly disrupted.

b. Substantial Impact

A Substantial Impact implies that some firms in the sector will experience at least a moderate and in some cases a serious impact, and a significant portion (greater than 10 percent but less than 40 percent) of the production in the sector related to the controlled chemicals will be ended or significantly disrupted.

c. Moderate Impact

A Moderate Impact is defined as when a few firms in a sector will experience a moderate impact on sales or profits, and no more than a small portion (less than 10 percent) of the sector production related to the controlled chemicals will be ended or significantly disrupted.

d. Limited Impact

The Limited Impact category includes those situations in which the regulations would impact firms or chemical production in a sector only through small but nonetheless measurable increases in product prices. If a reduction in a chemical's production or the imposition of a tax results in a large increase in the chemical's price, the resulting product price increase in sectors continuing to use the chemical may result in some unit sales fall-off. Equipment upgrading to reduce emissions to the atmosphere would also raise product prices. While the magnitude of these price and sales changes have not been estimated, the instances when they may occur have been identified by this impact category.

e. No Impact

The No Impact category covers instances when the proposed regulations would have essentially no impact on the firms or production of a particular sector related to the controlled chemicals. Very small price increases are possible under this category but not enough to affect sales.

Discussion of Economic Impact

An immediate ban on the use of the controlled chemicals (option a) would result in a severe and substantial impact on the users of the compounds. The aerosol industry would not be able to produce adequate supplies of substitute products within six months and thus the aerosol marketers would be affected substantially. While such a ban may prove to be a boon to producers and marketers of substitute products, this would be more than offset by the impact on producers, marketers and others connected with the aerosol industry.

The immediate ban would have a very severe impact on the refrigeration and air conditioning industry, especially if both F-12 and F-22 are banned. If F-22 could still be used, though, that portion of the industry using this compound would be unaffected. However, a conversion to F-22 or some other system by the rest of the industry, or better containment and servicing methods, could not be instituted within six months and probably not before a two to three year period.

While the cessation of production of the controlled chemicals would represent a substantial blow to the basic chemical producers, the overall impact on the companies has been categorized as moderate because the sales of the controlled chemicals do not represent a major portion of the companies' total business activity.

Options b and c would have the same impact on the aerosol industry and most other sectors as option a since the ban of the use of fluorocarbons as aerosol propellants is immediate. However, the impact of these options on the refrigeration industry is considerably lessened because the use of fluorocarbons as refrigerants is not banned. Under option b, though, the regulation would need to take effect after one year instead of six months in order for the impact to be lessened since it will take industry a minimum of one year to manufacture equipment with tighter leakage specifications. Option c will have no impact on the refrigeration industry.

The impact resulting from option d would tend to have the same influence on the various industry sectors as the previous two options. With production curtailed, demand will outstrip the available supply. This will in turn drive up prices, which could be substantial depending on on the resulting level of production. The fluorocarbon production would then be allocated to the highest bidder. Table B-7 indicates the percentage of the final product price represented by the cost of the chemical used in the products. As can be seen, the cost of the propellant (typically fluorocarbons) accounts for 15-25% of the aerosol product costs, while the cost of the refrigerant is an insignificant portion of the total product price. As a result, refrigeration applications would be more likely to sustain a large price increase of fluorocarbon prices than would aerosols, where cheaper substitutes already exist. Furthermore, since refrigeration and air conditioning are much more critical use areas than aerosols, consumers would be more likely to pay for a given increase in refrigerator or air conditioner prices than for the same absolute price rise in aerosol sprays. Thus, option d would tend to eliminate the use of fluorocarbons in most aerosol sprays while encouraging containment and recovery of the more costly refrigerant in refrigeration systems.

Options e through i show that the magnitude of the economic disruptions resulting from restrictions on the use of the chemicals is critically dependent on the timing of the restrictions. Under these options the chemical producers, substitute product producers, and the consumers of the chemicals have a longer response time avail-

Table B-7. VALUE OF FLUOROCARBONS
RELATED TO PRICES OF END-USE PRODUCTS (1973)

Chemical	Consuming Product	Cost of Chemical/Price of Product
F-11, F-12	Propellant Applications[a]	
	hair spray	15-20%
	antiperspirant	20-25%
	Intermediate Applications	
Carbon Tetrachloride	F-11, F-12	35-40%
	Refrigerant Applications	
F-11, F-12, F-22	appliances	0.1% - 0.2%
	mobile air conditioner	1-2%
	room and house air conditioner	0.2%
	commercial chiller	
	< 100 tons	0.1-1%
	> 100 tones	3%
	Blowing Agent Applications	
F-11, F-12		5%

[a] Based on manufacturer's price

Source: Arthur D. Little, Inc., estimates

able (three to six years) to bring on new products and thus ease the economic impact.

In the event of promulgation of any of these latter hypothetical options, the aerosol industry would have time for a response with substitute products since fluorocarbons would be banned. The impact on aerosol marketers would be limited because while their product line would undergo drastic change, their continuity of participation in their primary markets would not be interrupted. For the rest of the aerosol industry (fillers, valve manufacturers, etc.), the potential impact has a range of uncertainty because the availability of substitutes after three years is uncertain. If they were not available, the impact would be substantial while if they were available the impact would be moderate. The substantial classification indicates that the potential exists for very serious curtailment of their activities but the three year lead time would allow for some action to reduce the effects.

The impact of a ban on the use of fluorocarbons after three years would have a severe to substantial impact on the refrigeration and air-conditioning industry. If the use of F-22 was not restricted, the manufacturer's response to a ban on F-12 would be a conversion to F-22, which could be substantially completed by the end of three to five years. In the event F-22 could not be used, then conversion to other systems or refrigerants could not be completed by the end of three years; hence, the impact on the industry would be substantial.

The impact of options f through i would be relatively minor. The aerosol industry would be impacted to the same degree as under option e, but the other consuming sectors would have only a slight impact. For the basic chemical manufacturers, the impact of regulations at the end of three years is only slightly less than that of immediate action. While three years would allow time for the companies to work on substitute chemicals for major markets, new chemicals likely can not be tested and their production facilities brought on line within this period. Option i would have the slightest impact of any of the options since six years appears to be ample time for all sectors of the affected industries to adjust to the regulations and switch to substitute products or otherwise reduce emissions.

As previously indicated, this economic impact assessment does not provide a summation of the impacts on the various sectors. A small impact in many sectors could lead to a substantial impact on the overall economy or a segment of the economy. In addition, a large impact on a small number of industry sectors may not be large enough to create a substantial impact on the overall economy or a segment of the economy. Only by quantifying these impacts can the absolute extent of the various impacts on the industry sectors be determined. With this information available, the component impacts can be summed and the overall impact on the economy assessed.